F 1503/2

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI

040722

Tomul XXX (XXXIV)

Fasc. 1—4

Secţia II

CHIMIE ŞI INGINERIE CHIMICĂ

1984

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI

ORSZÁFOS MŰSZAKI INFORMÁCIÓS HÖZPONT ÉS KÖNYVTÁR 1883

Tomul XXX (XXXIV)

Fasc. 1 — 4

Secţia II

CHIMIE ŞI INGINERIE CHIMICĂ

1984

COLEGIUL DE REDACȚIE

Prof. dr. doc. **VAL. BLIDARU**
Prof. dr. doc. **N. V. BOȚAN**
Prof. dr. ing. **GH. CAȘLER**
Prof. dr. ing. **M. GAFIȚANU** (președinte)
Prof. dr. **P. MÂLCOMETE**
Prof. dr. doc. **D. MANGERON**
Prof. dr. ing. **T. SILION**
Acad. prof. dr. doc. **CR. SIMIONESCU**
Prof. dr. ing. **I. VLAD**

Prezenta fascicolă a fost tipărită cu sprijinul material al Comitetului sindical și al Consiliului U.A.S.C.R., Institutul politehnic, Iași.

COMITETUL DE REDACȚIE AL SECȚIEI II. CHIMIE ȘI INGINERIE CHIMICĂ

Prof. dr. ing. **N. ASANDEI**
Prof. dr. doc. **MAGDA PETROVANU**
Prof. dr. doc. **RADU TUDOSE**

REDACȚIA

Prof. dr. doc. **D. MANGERON**
(redactor responsabil)
Prof. dr. ing. **HUGO ROSMAN**
(secretar)
ECATERINA IRIMIEA
(tehnoredactor)

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
BULLETIN OF THE POLYTECHNIC INSTITUTE OF JASSY
ИЗВЕСТИЯ ЯССКОГО ПОЛИТЕХНИЧЕСКОГО ИНСТИТУТА
Tomul XXX (XXXIV), fasc. 1–4 1984

Secţia II

CHIMIE ŞI INGINERIE CHIMICĂ

SUMAR

Pag.

AL. CECAL, Studiul fenomenului de sorbţie a apei şi a etanolului pe cationiţi de tipul Dowex 50W încărcaţi cu ioni de Th^{4+} şi UO_2^{2+} utilizînd metoda isopiestică (engl., rez. rom.) 7

N. FOCA, O. VICOL şi N. HURDUC, Combinaţii complexe ale Pd (II) cu 2-amino tiophen (engl., rez. rom.) 13

V. DULMAN şi V. IACOB, Acumularea Ga(III) cu colectori microbiologici (*Spicaria Violacea*) (engl., rez. rom.) 19

M. FURNICĂ, Metodă polarografică pentru determinarea *o*-fenilendiaminei (rom., rez. franc.) 25

I. PÂRVU şi R. VASILIU, Aspecte cinetice ale electrorafinării intensive a stibiului în mediu de SbF_3 cu exces de H_2SO_4 şi HF (rom., rez. engl.) 29

P. ONU, GH. MIHĂILĂ, N. BÎLBĂ, C. LUCA şi D. GÎNJU, Anhidrizarea unor solvenţi organici pe tufuri vulcanice (engl., rez. rom.) 33

A. POPA, A. BOLD, GH. MIHĂILĂ, M. CRUCEANU şi E. POPOVICI, Separarea fierului, cromului şi zincului dintr-un catalizator oxidic uzat (engl., rez. rom.) 39

L. IFRIM, C. LEONTE, AL. SZÉP şi C. CALISTRU, Cercetări de inginerie chimică în cadrul procesului de obţinere a $Mg(OH)_2$ (II) (engl., rez. rom.) 43

AL. SZÉP, C. CALISTRU şi L. IFRIM, Cercetarea procesului de sublimare a clorurii de amoniu (I) (rom., rez. engl.) 51

GH. CRISTIAN, C. ONISCU, I. MIHALY şi I. IŞTOAN, Studii de cinetica uscării acidului fenoxiacetic (engl., rez. rom.) 61

A. AZZOUZ (Algeria), M. MACOVEANU şi I. HÂNCU, Purificarea acidului clorhidric într-o instalaţie de desorbţie—absorbţie (franc., rez. rom.) . . . 67

M. CAPROŞU, M. UNGUREANU şi M. PETROVANU, Piridaziniu-ilide (XII) (franc., rez. rom.) 73

I. COCÎRLĂ, C. I. GHIRVU şi L. PĂUNESCU, Asupra spectrelor electronice cu transfer de sarcină ale compuşilor obţinuţi din roşu neutru şi acid picric, acid barbituric, fenobarbital (engl., rez. rom.) 77

S. OPREA, E. DUMITRIU, M. STRUGARIU (R. S. România) şi A. AZZOUZ (Algeria), Studii privind selectivitatea catalizatorilor polifuncţionali în procesul de disproporţionare a toulenului (franc., rez. rom.) 83

C. VASILIU-OPREA, Sinteza mecano-chimică a compuşilor macromoleculari (rus., rez. rom.) 89

RECENZII 101

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
BULLETIN OF THE POLYTECHNIC INSTITUTE OF JASSY
ИЗВЕСТИЯ ЯССКОГО ПОЛИТЕХНИЧЕСКОГО ИНСТИТУТА
Tom XXX (XXXIV), Fasc. 1–4 1984

Section II

CHEMISTRY and CHEMICAL ENGINEERING

CONTENTS

Pp.

AL. CECAL, Study on the Phenomenon of Water and Ethanol Sorption on Cationites of the Type Dowex 50W Charged with Th^{4+} and UO_2^{2+} Ions Using the Isopiestic Method (English, Romanian summary) 7

N. FOCA, O. VICOL and N. HURDUC, Complexes of Pd(II) with 2-Aminotiophen (English, Romanian summary) 13

V. DULMAN and V. IACOB, Ga(III) Accumulation with Microbiological Collectors *(Spicaria Violacea)* (English, Romanian summary) 19

M. FURNICĂ, Méthode polarographique pour la détermination de l'*o*-phénylènediamine (Romanian, French summary) 25

I. PÂRVU and R. VASILIU, Kinetic Aspect of Intensive Electrorefining of Antimony in a SbF_3 Medium with H_2SO_4 and HF in Excess (Romanian, English summary) 29

P. ONU, GH. MIHĂILĂ, N. BÎLBĂ, C. LUCA and D. GÎNJU, Water Removal from some Organic Solvents on Volcanic Tuffs (English, Romanian summary) 33

A. POPA, A. BOLD, GH. MIHĂILĂ, M. CRUCEANU and E. POPOVICI, Separation of Iron, Chrome and Zinc from a Waste Oxidic Catalyst (English, Romanian summary) 39

L. IFRIM, C. LEONTE, AL. SZÉP and C. CALISTRU, Chemical Engineering Researches on the Process of $Mg(OH)_2$ Preparation (II) (English, Romanian summary) 43

AL. SZÉP, C. CALISTRU and L. IFRIM, Study of the Ammonium Chloride Sublimation Process (I) (Romanian, English summary) 51

GH. CRISTIAN, C. ONISCU, I. MIHALY and I. IŞTOAN, Studies on Kinetics of Phenoxyacetic Acid Drying (English, Romanian summary) 61

A. AZZOUZ (Alger), M. MACOVEANU et I. HÎNCU, Purification de l'acide chlorhydrique technique dans une installation desorbeur–absorbeur (French, Romanian summary) 67

M. CAPROŞU, M. UNGUREANU et M. PETROVANU, Pyridazinium-Ylures (XII) (French, Romanian summary) 73

I. COCÎRLĂ, C. I. GHIRVU and L. PĂUNESCU, On the Charge Transfer Electronic Spectra of the Compounds Obtained from Neutral Red and Picric Acid, Barbituric Acid, Phenobarbital (English, Romanian summary) 77

S. OPREA, E. DUMITRIU, M. STRUGARIU (R. S. Roumanie) et A. AZZOUZ (Alger), Études sur la séléctivité des catalyseurs polyfonctionnels dans le processus de disproportionnation du toluène (French, Romanian summary) 83

C. VASILIU-OPREA, Mechanochemical Synthesis of Macromolecular Compounds (Russian, Romanian summary) 89

BOOK REVIEWS 101

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
BULLETIN OF THE POLYTECHNIC INSTITUTE OF JASSY
ИЗВЕСТИЯ ЯССКОГО ПОЛИТЕХНИЧЕСКОГО ИНСТИТУТА
Том XXX (XXXIV), Вып. 1–4 1984 г.

Секция II

ХИМИЯ и ХИМИЧЕСКАЯ ПРОМЫШЛЕНОСТЬ

СОДЕРЖАНИЕ

Стр.

АЛ. ЧЕКАЛ, Изучение поглощающего явления воды и этанола на катиониты типа Дауэкс 50W заряженным ионнами Th^{4+} и UO_2^{2+}, используя изопиестический метод (англ., рез. рум.) 7
Н. ФОКА, О. ВИКОЛ и Н. ХУРДУК, Комплексы Pd(II) с 2 аминотифенолом (англ., рез. рум.) 13
В. ДУЛМАН и В. ЯКОБ, Концентрирование Ga(III) с микробиологическими коллекторами (*Spicaria Violacea*) (англ., рез. рум.) . . . 19
М. ФУРНИКЭ, Полярографический метод для определения *о*-фенилендиамина (рум., рез. франц.) 25
И. ПЫРВУ и Р. ВАСИЛИУ, Кинетические аспекты интенсивного электрорафинирования антимония в среде SbF_3 избытком H_2SO_4 и HF (рум., рез. англ.) 29
П. ОНУ, Г. МИХЭИЛЭ, Н. БЫЛБЭ, К. ЛУКА и Д. ГЫНЖУ, Удаление воды из нескольких органических растворителей на вулканические туффы (англ., рез. рум.) 33
А. ПОПА, А. БОЛД, Г. МИХЭИЛЭ, М. КРУЧЯНУ и Е. ПОПОВИЧ, Разделение железа, хрома и цинка из одного окисного изношенного катализатора (англ., рез. рум.) 39
Л. ИФРИМ, К. ЛЕОНТЕ, АЛ. СЕП и К. КАЛИСТРУ, Исследование процесса получения $MG(OH)_2$ (II) (англ., рез. рум.) 43
АЛ. СЕП, К. КАЛИСТРУ и Л. ИФРИМ, Исследование процесса сублимация хлорида аммония (I) (рум., рез. англ.) 51
Г. КРИСТЯН, К. ОНИСКУ, И. МИХАЛИ и И. ИШТОАН, Кинетические исследования сутки фенокси-уксусной кислоты (англ., рез. рум.) 61
А. АЗЗУЗ (Алжир), М. МАКОВЯНУ и И. ХЫНКУ, Очистка технической соляной кислоты на установке десорбций– абсорбций (франц., рез. рум.) 67
М. КАПРОШУ, М. УНГУРЯНУ и М. ПЕТРОВАНУ, Пиридазиниевые илиды (XII) (франц., рез. рум.) 73
И. КОКЫРЛЭ, К. И. ГИРВУ и Л. ПЭУНЕСКУ, О нагрузко-обменных спектрах соединении, полученных из красного неитрального и пикриного барбитурика кислот, фенобарбитала (англ., рез. рум.) 77
С. ОПРЯ, Е. ДУМИТРИУ, М. СТРУГАРЮ (Р.С.Р.) и А. АЗЗУЗ (Алжир), Изучение селективности полифункциональных катализаторов процесса диспропорционирования толуола (франц., рез. рум.) 83
К. ВАСИЛИУ-ОПРЯ, Механохимический синтез высокомолекулярных соединений (рус., рез. рум.) 89
РЕЦЕНЗИЙ 101

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secția II
CHIMIE și INGINERIE CHIMICĂ

D.C. 661.183.123.2

STUDY ON THE PHENOMENON OF WATER AND ETHANOL SORPTION ON CATIONITES OF THE TYPE DOWEX 50 W CHARGED WITH Th^{4+} AND UO_2^{2+} IONS USING THE ISOPIESTIC METHOD

BY

AL. CECAL

1. Introduction

The elucidation of the sorption phenomenon of some solvents on ion exchanger resins of different types and with several crosslinkings has preccoupied a series of researchers.

Thus Nandan and others [1], [2] have initiated a study concerning the elucidation of the mechanism of water and methanol sorption on ion exchangers of the sulphonic polystyrene type, charged with H^+, Li^+, Na^+ and K^+, with various percentages of divinyl benzene. Gregor and coworkers [3] as well as Boyd and Soldano [4] have studied the processus of water sorption on resins Dowex 50WX12 and Dowex 50WX13, concluding from the different forms of the respective isotherms, that the keeping of the solvent on the resin depends on the crosslinking of the respective ion exchanger.

The interactions ion—solvent and ion—ion, which are being produced at the same time with the sorption of the solvent on resin, have represented the subject-matter of different works [5]...[7], the authors of which have concluded that these interactions depend on the nature of the solvent, on the type and size of the ions linked to the respective ionit, on the pH-value, on the presence of some electrolytes etc.

In this paper we have initiated a comparative study on the process of water and ethanol sorption on ion exchanger resins of the type Dowex 50W with 2, 4, 8, 10 and 12% divinyl benzene, charged with Th^{4+} and UO_2^{2+} ions. For this purpose we have used the isopiestic method which has the advantage of being relatively simple, convenient, need not special apparatus, has a considerable accuracy and is much more efficient as compared to other procedures used in this respect. In fact, the isopiestic method is adequate both to the study of the sorption isotherms of some solvents on solid substances and to the study of the forming of complex compounds in the ternary systems.

2. Isopiestic Experiments

In order to carry out the experiments, we have taken 200 g of ion exchanger resins of the type Dowex 50WX2, 50WX4, 50WX8, 50WX10 and 50 WX12, which have been introduced in glass cylindrical columns of adequate dimensions for eluting. Thus each cationite has been treated with 1 000 ml NaOH solution (2 N), 1 000 ml water and 1 000 ml HNO_3 solution (2 N), after which an abundant washing with water and methanol followed.

In the end, the respective resins have been slowly eluted with 2 000 ml HNO_3 solution (2 N), after which they have been taken out of the glass columns and have been filtered through B ü c h n e r funnels. The resins, under the form of H^+, kept on the respective filters, have been repeatedly washed with water until the pH of the filtered substance has roughly attained the neutrality point value.

The cationites previously processed into (with a view to their subsequent charging with Th^{4+} and UO_2^{2+}) have been dried at 130°C, for 24 hours and have been stored in a dissicator, in vacuum, containing phosphorus pentoxide.

In order to determine the exchange capacity for each of the ion exchanger resins of the type Dowex 50W, as H^+ and with various percentages of divinyl benzene (2; 4; 8; 10 and 12%) we have taken approximatively equal quantities (1 g) out of these and we have introduced them in glass columns of small dimensions. Each cationite has been eluated with a certain known quantity of NaOH solution (0.1 N) and the excess has been titrated with solution of HCl (0.1 N). Out of the calculations we have then found the following values of exchange capacities (in g-ion H^+/g dried resin) of the exchange resins we have used : 5.2 for Dowex 50WX2 and Dowex 50WX4, 5.1 for Dowex 50WX8 and 5.0 for Dowex 50WX10 and Dowex 50WX12.

With a view to charge the respective resins with Th^{4+} and UO_2^{2+} ions, in adequate glass columns, they have been repeatedly eluted with concentrated solutions of thorium and uranyl nitrats in an acid medium. Then, the resins under the form of R_4Th and R_2UO_2, have been repeatedly washed with water, filtered through B ü c h n e r funnels and dried at 120°C, for 24 hours. They have also been deposited in a dissicator, in vacuum, with P_2O_5.

In order to verify if the utmost charge with Th^{4+} and UO_2^{2+} ions of the above mentioned cationites has been reached, 2 g of each have been taken. After eluting them, in adequate glass columns, with HNO_3 solution (2 N), the Th^{4+} and UO_2^{2+} ions have been moved away and have afterwards been gravimetrically dosed as ThO_2 and U_3O_8 [10]. The results of these measurements have confirmed the fact that an utmost charge with Th^{4+} and UO_2^{2+} ions of the respective resins has been practically reached, in all cases error being under 5%.

The isopiestic experiments have been made as follows :

For each type of cationite charged with ions of Th^{4+} and UO_2^{2+}, at which we have observed water and ethanol sorption, we have taken a vacuum dissicator with a lateral tube provided with a top, in which we have introduced a glass vessel, placed on the porcelain support, with apertures. The glass vessel contained a weighed quantity of one of the resins R_4Th or R_2UO_2 under study. At the bottom of each we have placed a capsule containing a solution of lithium chloride, in water or ethanol, having a certain concentration, in order to being about the wished activity of the respective solvent.

Then, by means of a diffusion pump, with adjustable flow capacity, through the lateral tube provided with a tap, a vacuum of 10^{-2} atm. has

been made inside each dissicator (during a 15 min. functioning of the pump), after which the connection with the vacuum outfit has been turned off.

In order to attain the sorption equilibrium of water or ethanol, on the resins under study, the samples have been maintained in the dissicator, which had been vacuumised for a week, at the constant temperature of 25°C, in a thermostated room. When this time interval was over, the lateral tap has been turned on so that air might slowly get into the dissicator. Then we have quickly weighed the respective samples, which as a result of the sorption phenomenon, have kept on the surface and inside the cationites a certain quantity of the given solvent. Taking into account the quantity of resin introduced at the beginning of the experiment, as well as the weight of the sample obtained after the solvent was kept, one can determine the quantity of water or ethanol in the cationite R_4Th or R_2UO_2 under study. Starting from here, one can calculate the number of moles of solvent which have been kept per miliequivalent of dried of the type Dowex 50W as Th^{4+} or UO_2^{2+}, with different crosslinkings.

We mention that during the opening of the dissicator and the weighing of the given sample a certain loss through evaporation of the solvent previously adsorbed on the cationite under study is inevitable being produced. But taking into account that each dissicator contain only one sample of cationite, at a certain activity of the solvent and that the experimental operations of opening of the dissicator and the weighing of a each sample have quickly followed each other in the same time interval, the error brought about by the evaporation of the absorbed solvent, up to the complete weighing is roughly the same in all cases and consequently, the experimental relative results which have been obtained may be considered correct. It is practically impossible to make such isopiestic experiments in the course of which any loss of solvent adsorbed on any solid sample be totally avoided

3. Results and Discussion

In order to establish the equivalence between the concentrations of the solutions of LiCl in water or in ethanol and the activities of these solvents, at 25°C, we have used the data from literature [11], which have been summarized up in Fig. 1.

We mention that the activity of the solvent represents the proportion of its pressure in the given solution and the pressure of its vapours in pure state, at the same temperature.

In Fig. 2 *a...d* we have graphically represented the sorption isotherms corresponding to water and to ethanol on ion exchanger resin) of the type Dowex 50W, with several percentages of divinyl benzene (2 ; 4 ; 8 ; 10 and 12%), charged

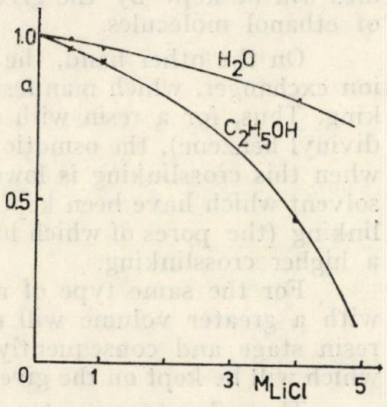


Fig. 1. The interdependence between the concentrations of the solution of LiCl in water and ethanol and the activities of the respective solvents.

with ions of Th^{4+} and UO_2^{2+} (separately). At 25°C these isotherms represent the interdependence between water or ethanol activity and the number of moles in the given solvent which have been retained per miliequivalent of dried resin, as Th^{4+} or UO_2^{2+}.

If we analyse the sorption isotherms, traced by means of the experimental data obtained through isopiestic measurements one may notice that :

a) The lower the crosslinking of the ion exchanger, the higher the number of moles of solvent which have been kept per miliequivalent of dried resin, a thing which is true for water or ethanol activities higher than 0.5.

b) Water sorption is much more obvious than ethanol sorption.

c) The volume and charge of the cation linked to the anionic rest of the resin influence differently the keeping of the solvent.

d) The *A* points positions (in Fig. 2) from which the „ramifications" of the sorption isotherms start, positions which are to be found at certain values corresponding both to the activity of the solvent and to the number of moles of solvent kept per miliequivalent of dried resin, depend on the nature of the solvent we used and on the size and charge of the cation linked to the resin. Up to these points, i.e., up to less perceptible activities of the solvent, one cannot notice important differences as far as water or ethanol keeping on ion exchangers with different percentages of divinyl benzene are concerned.

The sorption of the solvent on an ion exchanger resin is due to two simultaneous processes : the solvation of the ions by the given solvent, due especially to the reactions ion—solvent and the osmotic pressure which is being exercised on the anionite or cationite under study.

Thus, due to a greater dipole-moment for water (1.84 Debye), than for ethylic alcohol (1.70 Debye) [12], a higher solvation of the cation and of the anionic rests of the given resin are being produced, by the former solvent as compared to the latter. Hence, a greater number of water molecules will be kept by the given ion exchanger as compared to the number of ethanol molecules.

On the other hand, the solvent exercises an osmotic pressure on the ion exchanger, which manifests itself differently, depending on its crosslinking. Thus, for a resin with a higher crosslinking (a higher percentage of divinyl benzene), the osmotic pressure inside the resin stage is weaker than when this crosslinking is lower. In this situation, the number of moles of solvent which have been kept, will be greater for a resin with a lower crosslinking (the pores of which have got greater dimensions), than for one with a higher crosslinking.

For the same type of resin, but for two different solvents, the one with a greater volume will exercise a lower osmotic pressure inside the resin stage and consequently, the number of molecules in this solvent, which will be kept on the given ion exchanger, will be also smaller.

Thus, due to a greater solvation of the ions by water and due to the higher osmotic pressure, it exercises inside the resin, it is normal (as it has been proved experimentally) that a greater number of molecules in this solvent be kept, by means of the complex phenomenon of sorption, on the

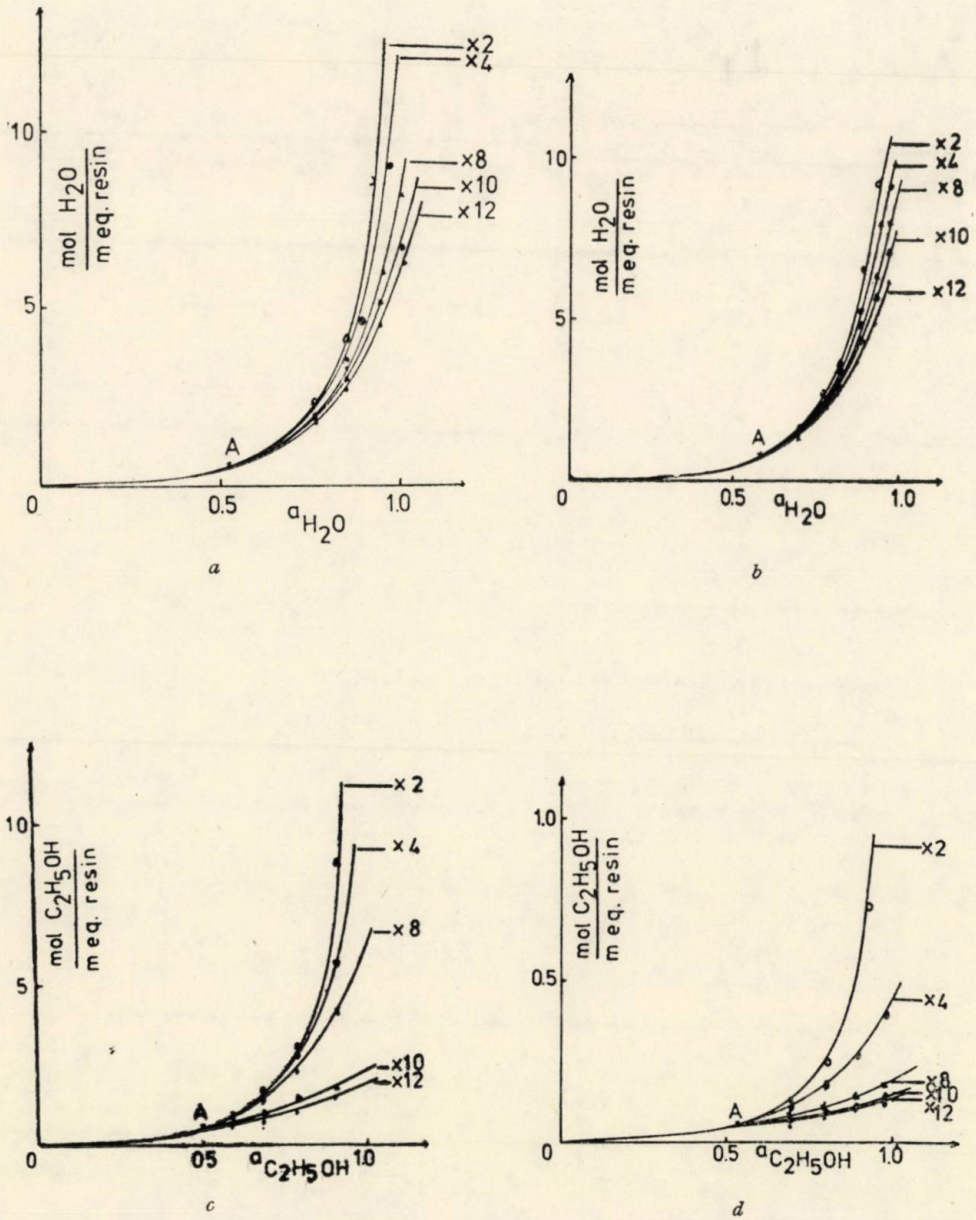
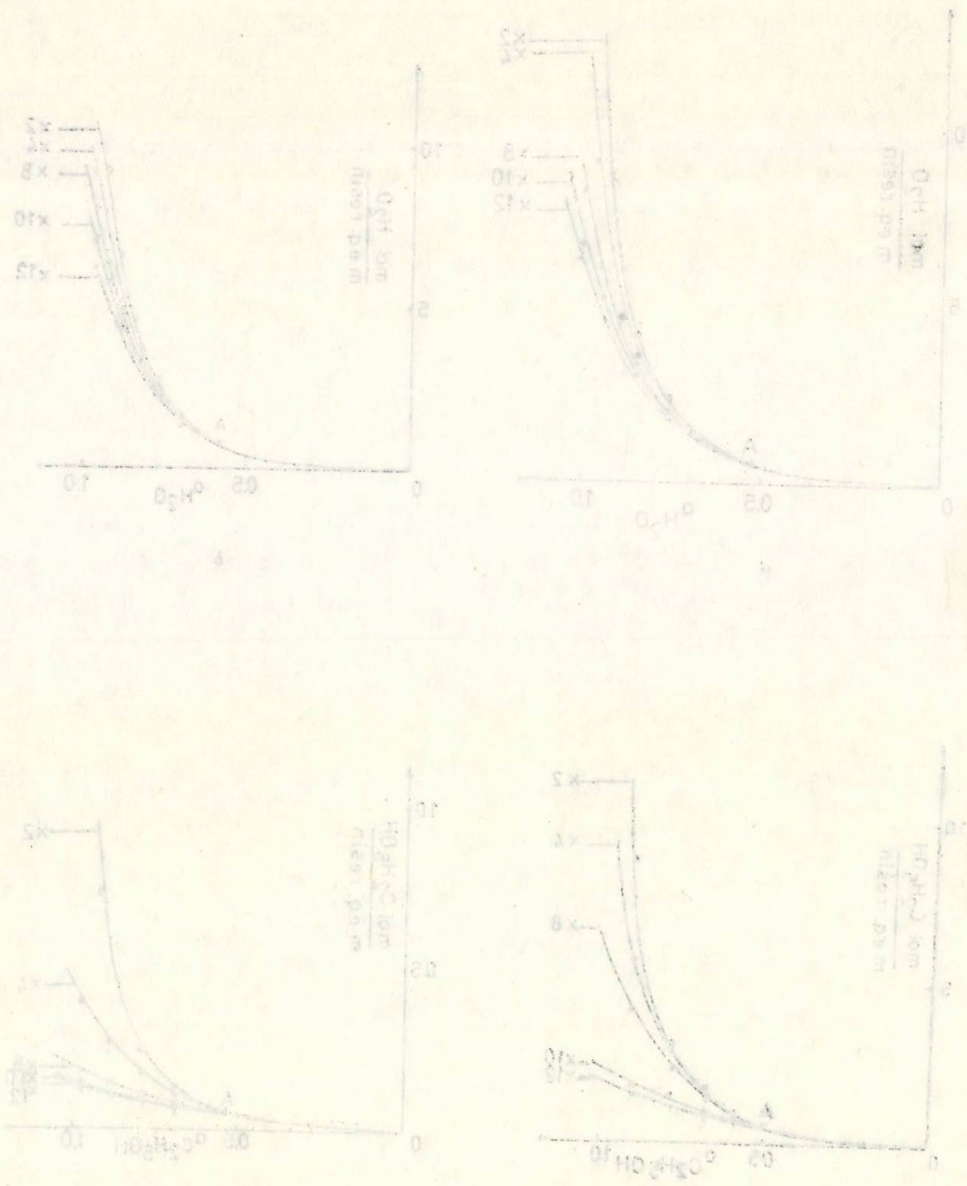


Fig. 2. — The sorption isotherms of water and ethanol, at 25°C, on ion exchangers of the type Dowex 50W, with different crosslinkings, charged with Th^{4+} and UO_2^{2+} ions : *a* — Water — R_4Th ; *b* — Water — R_2UO_2 ; *c* — Ethanol — R_4Th ; *d* — Ethanol — R_2UO_2.



respective ion exchanger, in comparison to the case of ethanol keeping on the same cationite.

The position of *A* point (for each of the Fig. 2), from which the „ramification" of the sorption isotherms of a solvent on a resin, with various crosslinkings is produced, may be regarded as a characteristic of the respective process, since this depends both on the solvent we used and on the cation linked to the anionic rests of the ion exchanger under study. Knowing from the diagram the position of this point, we can establish the value of activity of the solvent and implicitly of its number of moles, which have been kept per miliequivalent of dried resin, where the effects of the crosslinking of that cationite on the sorption processus begin to become distinct. This is rendered in Table 1.

Table 1

The Values of the Activities of the Solvent as well as of the Number of Moles in the same Solvent Kept per Miliequivalent of Dried Resin, Depending on the Nature of the Cation Contained in the Ion Exchanger, at the Position of the „Ramification" Point of the Sorption Isotherms

Resin / Activities and number of solvent moles	R_4Th	R_2UO_2
a_{H_2O}	0.55	0.65
$a_{C_2H_5OH}$	0.50	0.60
n_{H_2O}	0.60	0.50
$n_{C_2H_5OH}$	0.05	0.04

Out of the things presented above, one may concluded that the sorption phenomenon of a given solvent is more evident in the case of resins charged with ions of Th^{4+} than in the case of those containing UO_2^{2+} ions. If we study comparatively the results presented in this paper with those found by other authors [1] ... [4], referring to water sorption cations of the same type but charged with smaller ions, we may notice that the solvent is kept to a greater measure in this latter case than when the respective resins are charged with greater ions, i.e. Th^{4+} or UO_2^{2+}.

Received, January 20, 1982

Polytechnic Institute, Jassy, Department of Inorganic and Analytical Chemistry

REFERENCES

1. Nandan D., Gupta A. R., Shankar J., Indian J. Chem., **10**, 83 (1972).
2. Nandan, D., Gupta A. R., Indian J. Chem., **12**, 808 (1974).
3. Gregor H. P., Sundheim B. R., Held K. M., Waxman M. H., J. Colloid Sci., **7**, 511 (1952).

4. Boyd G. E., Soldano B. A., Z. Elektrochem., **57**, 162 (1953).
5. Coetzee J. F., Ritichie C. D., *Sclute—Solvent Interactions*. Marcel Dekker, New York, 1969.
6. Popovych O., Crit. Rev. Anal. Chem., **1**, 73 (1970).
7. Helfferich F., *Ion Exchange*. Mc Graw Hill, New York, 1962.
8. Вдовенко В. М., Рязанов М. А., Радиохимия, **8**, 519 (1966).
9. Кирпинцев А. Н., Лукянов А. В., Радиохимия, **6**, 449 (1964).
10. Vogel A. I., *Quantitative Inorganic Analysis including Elementary Instrumental Analysis*. Longmans, London, 1964.
11. Shaw R., Butler J. A. V., Proc. Roy. Soc., **129**, 519 (1930).
12. Reichardt C., *Effets de solvant en chimie organique*. Flammarion Sciences, Paris, 1971.

STUDIUL FENOMENULUI DE SORBŢIE A APEI ŞI A ETANOLULUI PE CATIONIŢI DE TIPUL DOWEX 50W ÎNCĂRCAŢI CU IONI DE Th^{4+} ŞI UO_2^{2+} UTILIZÎND METODA ISOPIESTICĂ

(Rezumat)

Se efectuează un studiu comparativ al sorbţiei apei şi a etanolului pe schimbători de ioni de tipul Dowex 50W, cu diferite grade de reticulare şi care sînt încărcaţi, separat, cu ioni de Th^{4+} şi UC_2^{2+}. Determinările experimentale au fost realizate prin metoda izopiestică. Din izotermele de sorbţie obţinute la 25°C s-au determinat atît activităţile cît şi numărul de moli din cei doi solvenţi de la care reţinerea lor pe răşini cu grade de reticulare diferite devine diferenţiată în funcţie de tipul solventului şi de natura cationului legat de acestea. Diferenţele legate de izotermele de sorbţie a apei şi a etanolului pe răşini schimbătoare de ioni de tipul Dowex 50W, cu 2 : 4 : 8 : 10 şi 12% divinil benzen au fost explicate luînd în considerare atît procesul de solvatare a ionilor de către aceşti solvenţi, cît şi presiunea osmotică pe care apa şi etanolul o exercită asupra răşinii respective.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secția II
CHIMIE ȘI INGINERIE CHIMICĂ

D. C. 661.898

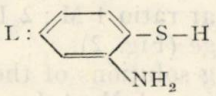
COMPLEXES OF Pd(II) WITH 2-AMINO-TIOPHEN

BY

N. FOCA, OLGA VICOL and NATALIA HURDUC

1. Introduction

The simple or complex combinations of Pd(II) : $PdCl_2$ and $K_2[PdCl_4]$ respectively, react in an acid or neutral medium with some organic compounds containing in their molecule the —SH group, leading to complex combinations as : $K[PdLCl_2]$; $[PdL_2]Cl_2$, where the ligand L is 2-amino tiophen (C_6H_7NS) [1] ... [3] :



The complex in the ratio 1 M : 2 L react with $K_2[PdCl_4]$ resulting a $[PdL_2]\,[PdCl_4]$ type complex.

The formation reactions of these complexes occur fast, since the very moment of mixing the reactants a precipitation of the above mentioned complex takes place in the solution.

2. Experimental

In this study a $PdCl_2$ solution was used, as obtained by dissolving $PdCl_2$ in HCl and diluting with water, in such a manner that the pH index should remain 1...2.

The solution with this pH index contains the complex ion $[PdCl_4]^{2-}$.

In same stages of the study the $K_2[PdCl_4]$ complex heshly solved in water was used.

The solution of the ligand 2-amino tiophen (L) was prepared by solving in C_2H_5OH 96% ; 2-amino tiophen is soluble only in organic solvents such as :

$$C_6H_6,\ CH_3—\underset{\underset{O}{\|}}{C}—CH_3,\ CCl_4,\ CHCl_3,\ CH_3OH \text{ and so one.}$$

The solutions of Pd(II) and 2-amino tiophen had concentrations between 1×10^{-2} and 1×10^{-3} mol/l. By dilution with water for Pd(II) or with C_2H_5OH for the ligand, the desired concentrations were obtained.

2. Results and Discussions

The Pd(II) ion reacts with 2-amino tiophen resulting complex combinations heaving a characteristic spectrum in the UV and visible range, as shown in Figs. 1 and 2.

The 2-amino tiophen-ligand in ethilic alcohol ($c=5.10^{-5}$ mol/l) shows a simple spectrum, that is just one band in the ultraviolet range ($\lambda_{max}=$ $=204$ nm).

The metallic ion, that is $PdCl_2$ ($c=2\times 10^{-4}$ mol/l), shows three absorbtion bands in the UV range, characterized by $\lambda_{max}=215$, 242, 320 nm [4].

From the reaction between 2-amino tiophen and Pd(II) in C_2H_5OH arise complexes showing absorbtion spectra both in the UV and visible range. Thus, the complex with the molar ratio 1 M : 1 L shows in the ultraviolet range a single band with $\lambda_{max}=212$ nm, while that with the molar ratio 1 M : 2 L shows, besides the band with $\lambda_{max}=212$ nm, a shoulder at $\lambda_{max}=250$ nm.

The absorbtion of the free ligand ($PdCl_2$) and of the two new obtained complexes are plotted in Fig. 1.

$PdCl_2$, $K_2[PdCl_4]$ and 2-amino tiophen reactants does not show absorbtion bands in the visible range of the spectrum, for the concentrations we used.

The complexes with molar ratio 1 M : 2 L show characteristic absorbtion spectra in the visible range (Fig. 2).

Records were made using solutions of the $PdCl_2$ and 2-amino tiophen with the following molar ratios : 1 M : 1 L ; 1 M : 2 L ; 1 M : 3 L and 1 M : 4 L, in alcoholic medium (80% C_2H_5OH and 20% water) ; the concentration of the metal ion, Pd(II), respectively $c = 2\times 10^{-4}$ mol/l in $PdCl_2$, was held constant.

The spectra were recorded both simultaneously with the mixing of the reactants and 30 min. later.

From the recordings a crossing of the spectra appears at $\lambda_{max}=395$ nm (Fig. 2). The crossing point of the absorbtion curves similar to an isobestic is due either to the equilibrium of different complex species, wich is true isobestic, or to the precipitation of the 1 : 2 and 1 : 1 complexes produced by the excess of the ligand (Fig. 2) ; this complex separation makes the solutions containing ligand in excess to show less absorbance for $\lambda_{max}=395$ nm.

The recordings were made on a Spekord UV - vis (GDR) automatic spectrophotometer, in 0.2 cm think cuves, with a wittness mixture compared of four parts C_2H_5OH and one H_2O.

The complexes of Pd(II) with 2-amino tiophen have been prepared by mixing the solutions of the reactants (2-amino tiophen in alcoholic solution 96%, $c = 1\times 10^{-2}$ mol/l and a solution of $K_2[PdCl_4]$ in a quantity of water as small as possible) in stoechiometric ratios (1 M : 1 L and 1 M : 2 L).

The separation of these compounds can also be done using solutions of the ligand in other organic solvents such as C_6H_6, $C_6H_5-CH_3$, CCl_4 a.s.o.

The alcoholic solution of the ligand is advantageous because this solutions mixes well with the aqueous $K_2[PdCl_4]$. On the other hand, the use of the aqueous solution of $K_2[PdCl_4]$ using small amounts of water is also important as 2-amino tiophen is rather very soluble in water after

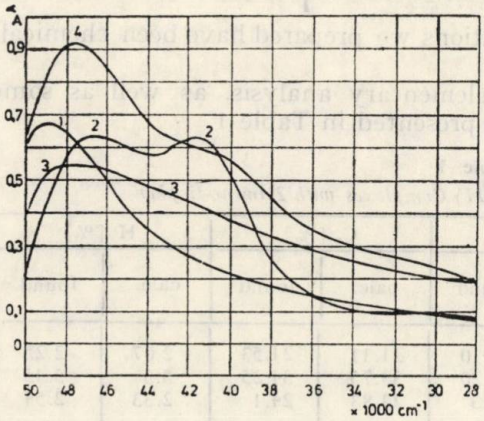


Fig. 1. — Electronic spectra (UV) of the reactants and of the reaction products in the Pd(II) —2-aminotiophen system : *1* — 2 amino-tiophen (L) in ethylic alcohol, $c = 1 \times 10^{-4}$ moles/l, layer depth 0.2 cm ; *2* — $PdCl_2$ in ethylic alcohol, $c = 2 \times 10^{-4}$ moles/l, layer depth 0.5 cm ; *3* — $PdCl_2$ + L(1 : 1) in ethylic alcohol, $c = 1 \times 10^{-4}$ moles/l in $PdCl_2$, layer depth 0.2 cm ; *4* — $PdCl_2$ + 2L(1 : 2) in ethylic alcohol, $c = 1 \times 10^{-4}$ moles/l in $PdCl_2$, layer depth 0.2 cm.

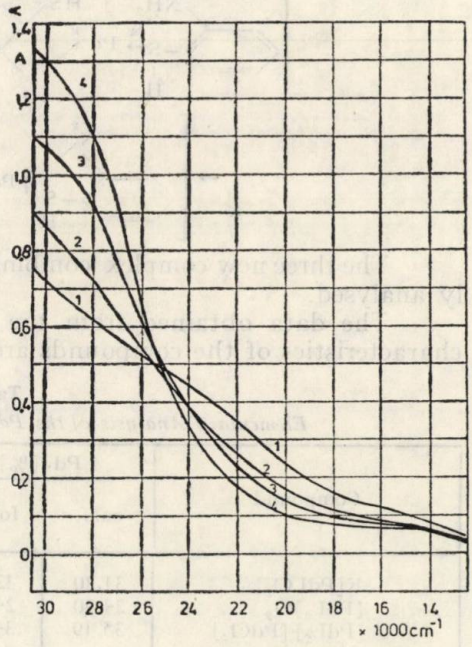
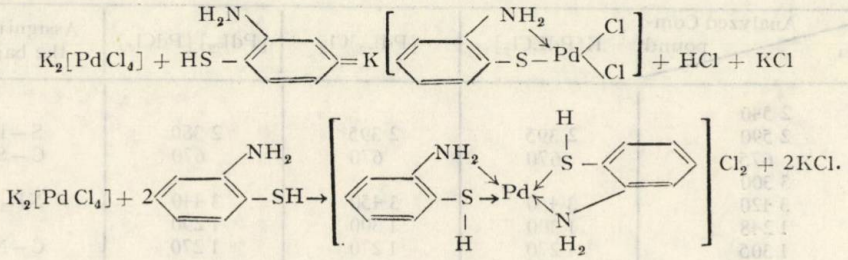


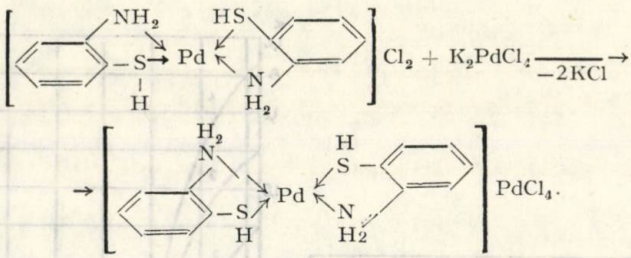
Fig. 2. — Electronic spectra (visible) of the reaction products in the Pd(II) —2-amino tiophen system, 30 min. after the reactants mixing (20 % H_2O and 80 % C_2H_5OH): *1* — $PdCl_2$ + L ; *2* — $PdCl_2$ + 2L ; *3* — $PdCl_2$ + + 3L ; *4* — $PdCl_2$ + 4L ; the initial concentration of the $PdCl_2$ solution : 1×10^{-3} moles/l ; the initial concentration of the ligand solution (2-amino tiophen) L: 1×10^{-3} moles/l; final volume 5 cm^3 ; layer depth 0.5 cm.

certains limits (40% water). After this limit the precipitation of the ligand from the solution takes place.

The formation of the complexes we prepared are probably the following :



The third compound ($[PdL_2]$ $[PdCl_4]$) is obtained by treating the $[PdL_2]$ Cl_2 complex with $K_2[PdCl_4]$ according to the reaction :



The three new complex combinations we prepared have been chemically analysed.

The data obtained from the elementary analysis, as well as some characteristics of the compounds are presented in Table 1.

Table 1

Elementary Analysis of the Pd(II) Complexes with 2Amino-tiophen

Compound	Pd, [%]		C, [%]		H [%]	
	calc.	found	calc.	found	calc.	found
$K[PdLCl_2]$	31.20	32.10	21.11	21.53	2.07	2.25
$[PdL_2]Cl_2$	24.90	24.20	33.75	34.25	3.3	3.45
$[PdL_2][PdCl_4]$	35.19	34.3	23.83	24.1	2.33	2.54

The infrared spectra of the synthesized complexes were recorded with UR-10 spectrophotometer.

The IR spectra of $K[PdLCl_2]$, $[PdL_2]Cl_2$ and $[PdL_2][PdCl_4]$ complexes were compared with those of the free ligand, taking into account the group characteristic frequencies.

The ligand (2-amino tiophen) shows vibrations which are characteristic to the proposed molecular structure in good agreement with the literature data [5], [6].

Comparing the IR spectra of the three new complexes with that of the free ligand it appears that the ν_{SH}, ν_{C-S}, ν_{NH_2} and ν_{CH} group characteristic frequencies are affected.

Table 2

Assignings of Specific IR Bands, [cm^{-1}]

Analyzed Compound / cm^{-1}	$K[PdLCl_2]$	$[PdL_2]Cl_2$	$[PdL_2][PdCl_4]$	Assigning of the bands
2 540				
2 590	2 395	2 395	2 380	S–H
675	670	670	670	C–S
3 300				
3 420	3 450	3 450	3 440	NH_2
1 248	1 300	1 300	1 290	
1 305	1 270	1 270	1 270	C–N
3 000	3 060			
3 045	3 030	3 050	3 070	C–H

This leads to the conclusion that the ligand in question used as coordinative points the $-NH_2$ and $-SH$ groups.

The complexes of Pd(II) with 2-amino tiophen have also been investigated by thermal analysis.

The recordings were made using a MOM—Budapest-type derivatograph for a heating rate of 12°C/min, with aluminium oxyde at 1 000°C as an etalon sample.

The thermograms we obtained suggest a thermal behaviour rather similar in two stages for the $[PdL_2]\,Cl_2$ and $[PdL_2]\,[PdCl_4]$ compounds.

A more complex thermal behaviour shows $K[PdLCl_2]$ as suggested by the greater number of stages.

The thermogravimetric characteristic as plotted in Table 3 confirm the formulations of the three new complex combinations.

Table 3

Thermogravimetrical Characteristics of Pd(II) —2-Amino-tiophen Complexes

Compound analyzed	Temperature range °C	Rezidue	mg	
			calc.	found
$K[Pd(C_6H_7NS)Cl_2]$	30...80, 220...260 260...390, 360...490	$PdCl_2$	9.8	9.2
$[Pd(C_6H_7NS)_2]Cl_2$	30...120 280...480	$PdCl_2$	7.6	7.2
$[Pd(C_6H_7NS)_2]\,[PdCl_4]$	30...200 350...490	PdS + $PdCl_2$	5.2	5.28

The analytical calculation would also suggest that the degradation starts by the elimination of some simple molecules, such as ammonia, leading to an intermediate product with sulphur bridges which later degradate the selves to $PdCl_2$ mechanism confirmed also for other Pd(II) complexes with ligands containing in their structures nitrogen and sulphur [6], [7]:

$$K[PdLCl_2] \xrightarrow{-NH_3} R_1 \xrightarrow{-H_2S} R_2 \rightarrow PdCl_2$$

$$K[Pd(C_6H_7NS)Cl_2] \xrightarrow{-NH_3} \begin{matrix} Cl \\ -S \end{matrix}\!\!>\!Pd\!<\!\!\begin{matrix} S- \\ Cl \end{matrix} \xrightarrow{-H_2S} PdCl_2.$$

Received June 15, 1982

Polytechnic Institute, Jassy,
Department of Inorganic and
Analytical Chemistry

REFERENCES

1. Vicol O, Hărăbor P., An. şt. Univ. „Al. I. Cuza", Iaşi, **20**, *1*, 117 (1974).
2. Vicol O., An. şt. Univ. „Al. I. Cuza", Iaşi, **20**, *2*, 152 (1974).
3. Neville G., Gorin G., J. Chem. Am, Soc., **78**, 4893 (1956).

4. Gray H. B., Balhausen J., J. Am. Chem. Soc., **85**, 260 (1963).
5. Balhausen C. J., Gray H. B., *Molecular Orbital Theory*. W. A. Benjamin, New York, 1964.
6. Nakamoto K., *Infrared Spectra of Inorganic and Coordination Compounds*. J. Wiley a. Sons, New York, 1963.
7. Vicol O., Hurduc N., Schneider I. A., J. Inorg. Nucl. Chem., **41**, 309–315 (1978).

COMBINAŢII COMPLEXE ALE Pd(II) CU 2-AMINO TIOFEN

(Rezumat)

Se studiază sinteza şi caracterizarea chimică a unor complecşi noi ai Pd(II) cu 2-amino tiofen.

Structura acestor compuşi a fost propusă pe baza analizelor spectrale (în domeniile U V vizibil şi IR) precum şi pe baza comportării lor termice.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

D.C. 546.681 ; 663

GA (III) ACCUMULATION WITH MICROBIOLOGICAL COLLECTORS *Spicaria Violacea*

BY

VIORICA DULMAN and VIORICA IACOB

1. Introduction

Microorganisms capable of accumulating and concentrating elements have been called „microbiological collectors" [1]. The fungus *Spicaria Violacea* displays characterics as a microbiological collector, being endowed with the capacity of concentrating isotopes, metallic ions from diluted solutions [2]...[4]. The study of some metalloenzymes is of interest for ellucidating the concentrating cations mechanisms from diluted solutions [5].

Gallium is an element necessary for the growth of microscopic fungi. For instance *Aspergillus niger* needs 0.5 μg Ga(III)/l for a maximum growth. Likewise, Ga (III) in smaller concentrations stimulates the growth and sporulation of fungi [7], [8].

The present paper aims at setting for the optimal conditions of Ga(III) concentration with *Spicaria Violacea* as a microbiological collector (pH, time, concentration Ga(III)), the influence of Al(III), Fe(II), Fe(III) in the process and the influence of Ga(III) on the biosynthesis of acid phosphatase.

2. Experimental

There has been used the fungus *Spicaria Violacea* kept and cultivated in the medium mentioned in previous papers [2], [3].

The standard solutions have been prepared from nitrate for Ga(III) and chlorides for Al(III) and Fe(III). Gallium have been spectrophotometrically determined with rhodamin *B* [9] and with aluminon for Al(III) [10].

The Specord UV — Vis (Zeiss) spectrophotometer has been used.

The analysis have been carried out on the ash obtained by heating the biomass of the fungus at 700°C. The ash has been treated with HCl 1 : 1 on a water bath and evaporated to dryness, then dissolved in HCl 1 : 1 and the solution thus obtained has been used for determinations. In order to separate Ga(III) from Al(III) in the presence of Fe(III), gallium has been extracted from the acid solution (HCl 6 N) with ethyl ether after a preliminary reduction of Fe(III) with $TiCl_3$ 15% [9].

The enzymatic activity of the acid phosphatase has been determined from the amount of anorganic phosphorus freed by the action of the enzymatic extract on buffer solution, pH = 6.2, of β sodium glicerophosphate, for 30 min., at 30°C. The activity has been rendered by microgrammes of phosphorus freed by the substrate and the specific activity in micrograms phosphorus freed by 1 mg protein enzyme [11].

3. Results and Discussion

3.1. The influence of pH

The optimum pH of the culture of gallium accumulation is 5.

3.2. The Influence of Time

This influence has been determined in two ways :

a) The inoculated samples that contain 0.89 μg Ga(III)/ml with the pH = 5 of the culture — medium have been collected at various time intervals. There can be found (Fig. 1, curve *A*) that the maximum accumulation of gallium occurs at 25 days of the fungus growth after which it keeps constant during the tested time interval.

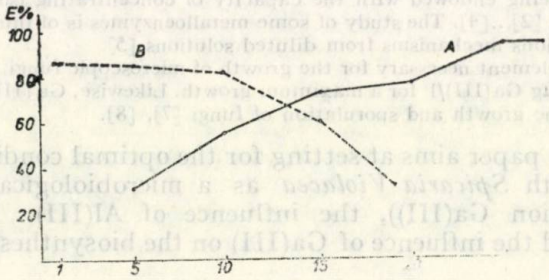


Fig. 1. — The influence of time on gallium concentration : *A* — collection of biomass at various time intervals ; *B* — Ga (III) addition at various stages of fungus growth.

b) By adding Ga(III) 0.89 μg/ml in various stages of the fungs growth, there can be shown that gallium is accumulated during the early stages of fungus growth (Fig. 1, curve *B*). This would plead for the fact that Ga(III) partakes of processes within the cell.

3.3. Influence of Gallium Concentration

At a pH = 5 gallium is concentrated for 25 days ~ 97% in the range of concentration 0.4 ... 2.6 μg/ml, after which the accumulation rate decrease reaching 59% at 536 μg Ga (III)/ml (Fig. 2).

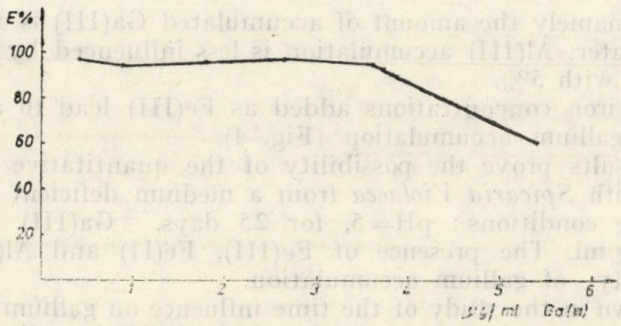


Fig. 2. — Influence of Ga(III) concentration on gallium accumulation.

3.4. Influence of Al(III) on Gallium Accumulation

Under the optimal conditions shown (pH=5, for 25 days, at a concentration of Ga(III) of 0.465 μg/ml), Al(III) has been added in various concentrations and one can notice that the presence of Al(III) leads to the decrease of gallium accumulation rate, reaching 22% for 1.84 μg Al(III)/ml (Fig. 3, curve *A*).

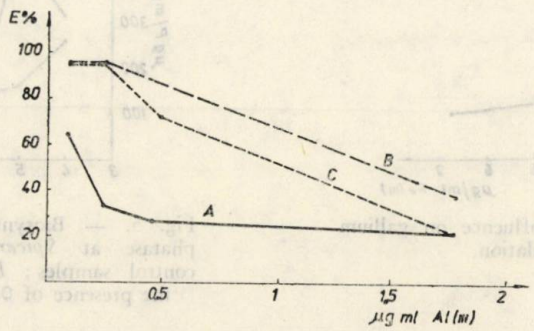


Fig. 3. — Al(III) influence on gallium accumulation: *A* — Ga(III) accumulation in the presence of Al(III); *B* — Accumulation of Al(III) present in various concentrations in the medium and with 0.465 μg Ga(III)/ml; *C* — Accumulation of Al(III) present in various concentrations in the medium when Ga(III) is absent.

Ga(III) stimulated but little Al(III) accumulation (Fig. 3, curve *B*) in comparison with accumulation when Ga(III) is absent (Fig. 3, curve *C*).

3.5. Fe (III) Influence on Ga (III) Accumulation

The preliminary testings on Ga(III) accumulation with *Spicaria Violacea* showed that this process unholds better in a medium deficient in iron, prepared without the addition of the adequate amount of ferrous

sulphate [1] namely the amount of accumulated Ga(III) is approximately two times greater. Al(III) accumulation is less influenced by Fe(II) proportion, namely with 5%.

Higher iron concentrations added as Fe(III) lead to a considerable decrease of gallium accumulation (Fig. 4).

The results prove the possibility of the quantitative concentration of gallium with *Spicaria Violacea* from a medium deficient in iron under the following conditions: pH=5, for 25 days, Ga(III) concentration 0.465...2.5 μg/ml. The presence of Fe(III), Fe(II) and Al(III) decrease the rentability of gallium accumulation.

As shown in the study of the time influence on gallium accumulation there can be supposed on inside of Ga(III) within the cells as a predominant phenomenon. The testings carried out on some enzymes (alcaline phosphatase, acid phosphatase, peroxidase, catalase) yielded positive results only for acid phosphatase. It is biosynthesised in cells of *Spicaria Violacea* and the amount of the issuing enzyme depends on the pH of the medium (Fig. 5, curve *B*). For a pH = 4 the activity of the enzyme is maximum.

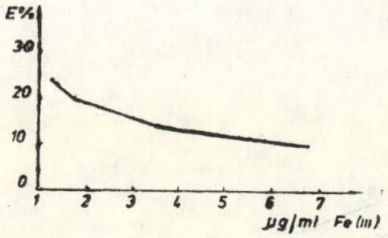


Fig. 4. — Fe(III) influence on gallium accumulation.

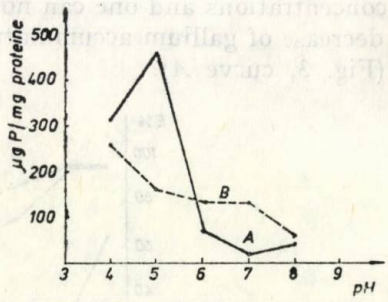


Fig. 5. — Biosynthesis of acid phosphatase at *Spicaria Violacea*: *A* — control samples; *B* — biosynthesis in the presence of 0.465 μg/ml Ga(III).

Gallium added to the culture medium 0.465 μg/ml has a favourable influence on the biosynthesis of acid phosphatase reaching values superior to the control samples between pH=4 and 5.8 displaying a maximum value at pH=5 while between pH=5.8...8 the biosynthesis of acid phosphatase is situated at values inferior to the control tests (Fig. 5, curve *A*).

Though the maximum accumulation of Ga(III) at pH=5 might be accounted for as also due to the activity of the acid phosphatase stimulated by this element.

The fact that Ga(III) accumulation decreases in the presence of Al(III) could be correlated with the partial replacing of Ga(III) by aluminium in its functions but whose action is not identical. It is known [7] that for gallium substitution salts of 76 elements have been experimented but no one could substitute Ga(III). Taking into account the some similary properties of Ga(III) and Al(III) it is assumed that the biological activity sometimes attributed to Al(III) might belong to Ga(III).

It is also known that transport system present in the microscopic fungus *Ustilago sphaerogena* for the ferric ion mediated by ferrichrom can transport about 70% of the complexes of aluminium and gallium by ferrichrom [12]. This system has been shown in the case of the fungus grown in a deficient medium in iron ; thus it is not quite out of the question that among the metabolism products of *Spicaria Violacea* there might exist compounds responsible for the transport of Ga(III).

4. Conclusions

1. It is possible to quantitatively accumulate Ga(III) with *Spicaria Violacea* as a microbiological collector, from a medium deficient in iron under the following conditions : pH = 5, for 25 days, concentration of Ga(III) from 0.465 to 2.6 μg/ml.

2. Al(III) (0.23...1.8 μg/ml) and Fe(III) (0.33...6.78 μg/ml) decrease the accumulation percentages of gallium.

3. The biosynthesis of acid phosphatase is stimulated at a pH = 5, in the presence of 0.465 μg/ml Ga(III) as compared with the test samples where Ga(III) was absent.

Received, March 22, 1982

Polytechnic Institute, Jassy,
Department of Inorganic
and Analytical Chemistry

REFERENCES

1. Fișel S., Topală N. D., Țintaru V., IInd National Conf. on Anal. Chem., Brașov, 4, 1971, 425.
2. Fișel S., Dulman V., Cecal Al., J. Radioanal. Chem., **27**, 83 (1975).
3. Fișel S., Dulman V., Cecal Al., J. Radioanal. Chem., **34**, 285 (1976).
4. Fișel S., Dulman V., Rev. Chim., **28**, 286 (1977).
5. Artenie V., Dulman V., Fișel S., St. cerc. biochim., **21**, 11 (1978).
6. Bertrand D., Wolf A., Bull. Soc. Chim. Biol., **38**, 959 (1956).
7. Yoe J. H., Koch H. J. (Ed.), *Анализ следов элементов* (пер. с англ.). ИИЛ, М., 1961.
8. Bertrand D., C. R. Acad. Sci., Paris, **239**, 1 706 (1954).
9. Demetrescu A., Tutoveanu A., Ionescu M., *Analiza tehnică a minereurilor*. Ed. Tehn., Buc., 1966, 490.
10. Sandell E. B., *Colorimetric Detemination of Traces of Metals*. IIIrd Ed., Interscience, New York, 1959, 475.
11. Artenie V., *Lucrări practice în chimia biologică*. Univ. „Al. I. Cuza", Iași, 1970.
12. Lankford C. E., Crit. Rev. Microbiol., **2**, 273 (1973).

ACUMULAREA GA(III) CU COLECTORI MICROBIOLOGICI (*Spicaria Violacea*)

(Rezumat)

Ciuperca *Spicaria Violacea* a fost utilizată în calitate de colector microbiologic pentru concentrarea Ga(III) din soluții diluate. În acest scop s-au studiat condițiile optime de pH, timp, concentrația Ga(III), care influențează acest proces. De asemenea s-a urmărit influența Al(III), Fe(II), Fe(III) asupra acumulării Ga(III) și biosinteza fosfatazei acide în prezența Ga(III).

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

C.Z. 545.33 ; 547.553.1

METODĂ POLAROGRAFICĂ PENTRU DETERMINAREA *o*-FENILENDIAMINEI

DE

M. FURNICĂ

1. Introducere

Literatura de specialitate cuprinde o serie de lucrări în care se cercetează oxidarea electrochimică a *o*-fenilendiaminei (*o*-FDA) pe diferiţi electrozi solizi, atît în scopul elucidării mecanismului procesului de electrod [1], [2], cît şi în scopul stabilirii condiţiilor optime pentru determinarea *o*-FDA [3], [4]. Din aceste studii rezultă că în anumite condiţii de pH, *o*-FDA se oxidează pe electrozii solizi din platină, aur, grafit, la forma diiminică, printr-un proces de electrod cu participarea a doi electroni, iar unda polarografică corespunzătoare acestui proces poate servi în scopuri analitice.

În cele ce urmează se cercetează posibilitatea folosirii metodei polarografice cu electrod picător de mercur la determinarea *o*-FDA, printr-o metodă indirectă, bazată pe oxidarea *o*-FDA cu ioni de Fe^{3+}, într-un compus activ polarografic.

Potrivit datelor din literatura de specialitate [5] ... [8] ionii de Fe^{3+}, în mediu acid (pH=2), oxidează cantitativ *o*-FDA în 2,3-diaminofenazină, care posedă proprietatea de a se reduce pe electrodul picător de mercur datorită nucleului fenazinic [9].

Într-o lucrare anterioară [10] au fost stabilite condiţiile experimentale pentru obţinerea undei de reducere a 2,3-diaminofenazinei pe electrodul picător de mercur, bine exprimată şi proporţională cu concentraţia. Aceste condiţii au fost realizate şi în prezenta lucrare.

2. Partea experimentală

2.1. Reactivi şi aparatura utilizată

o-FDA a fost purificată prin recristalizare din alcool etilic. Pentru efectuarea determinărilor s-au folosit soluţii apoase proaspăt preparate pentru a evita oxidarea parţială a *o*-FDA în timp.

Soluţia cu ioni de Fe^{3+}, necesară oxidării *o*-FDA, s-a preparat din alaun feriamoniacal în concentraţie de 0,01 M în H_2SO_4, pH=2.

Pentru prepararea soluţiei de bază s-au folosit următoarele soluţii : soluţie de $NaNO_3$ 1 N, soluţie de gelatină 0,25% şi soluţie tampon acid acetic — acetat de sodiu 0,2 N, pH=6, pentru stabilizarea pH-ului.

Oxigenul solvit în soluţia supusă polarografierii s-a îndepărtat prin trecerea unui curent de azot, timp de 10 min. Pentru purificarea azotului de urmele de oxigen s-a folosit o soluţie alcalină de pirogalol.

Ionii de Fe^{3+} în exces au fost complexaţi cu NaF 1 N , întrucît aceştia formează o undă la începutul polarogramei, care împiedică determinările.

Determinările polarografice au fost efectuate la un polarograf LP55. Ca electrod nepolarizabil s-a folosit electrodul de calomel saturat asociat cu celula polarografică printr-o punte electrolitică umplută cu agar-agar în soluţie saturată de clorură de potasiu.

pH-ul soluţiilor s-a determinat cu un electrod de sticlă la un pH-metru MV 85.

2.2. Modul de lucru

După o serie de investigaţii privind natura şi cantitatea de reactiv pentru complexarea ionilor de Fe^{3+} rămaşi după oxidarea *o*-FDA, cantitatea de *o*-FDA luată pentru determinare, timpul necesar eliminării oxigenului din soluţie, s-a stabilit următorul mod de lucru : într-un balon cotat de 25 ml se introduce un volum determinat din soluţia de *o*-FDA proaspăt preparată, în general 0,5 ... 3 ml soluţie 0,01 M, peste care se adaugă, încet şi sub agitare, 6 ml soluţie de alaun feriamoniacal 0,01 M, cînd soluţia de *o*-FDA se colorează în roşu intens ; se adaugă apoi 2,5 ml NaF pentru complexarea ionilor de Fe^{3+} în exces, 5 ml alcool pentru solvirea completă a 2,3-diaminofenazinei formată prin oxidarea *o*-FDA de către ionii de Fe^{3+} 2,5 ml $NaNO_3$, 1 ml gelatină, 5 ml soluţie tampon şi se completează la marcă cu apă distilată.

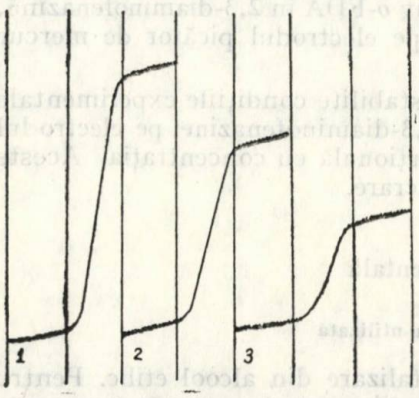


Fig. 1. — Undele polarografice ale soluţiilor de *o*-FDA oxidată cu Fe^{3+} : *1* — 1,2 ; *2* — 0,8 ; *3* — $0,4.10^{-3}$ M; tensiunea iniţială 0,2 V ; sensibilitatea galvanometrului 1/30.

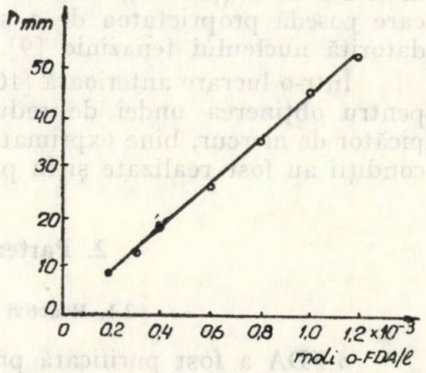


Fig. 2. — Variaţia înălţimii undei polarografice în funcţie de concentraţia soluţiilor de *o*-FDA.

Din soluția astfel obținută se extrag aproximativ 15 ml care se introduc în celula polarografică. Prin dopul celulei se introduc capilara electrodului picător de mercur, puntea electrolitică și tubul prin care se trece azot. După 10 min. de trecere a azotului se obține curba polarografică în domeniul de potențial cuprins între —0,2 V și —0,8 V cu o sensibilitate a galvanometrului de 1/30.

În aceste condiții forma undelor polarografice este bine exprimată și înălțimea lor este proporțională cu concentrația soluțiilor de *o*-FDA (fig. 1 și 2).

Pe baza experiențelor efectuate s-a constatat că reacția dintre *o*-FDA și Fe^{3+} are loc cantitativ în condițiile de lucru indicate mai sus numai dacă raportul Fe/*o*-FDA este de cel puțin 3 și nu mai mare de 15. Excesul ionilor de Fe^{3+} poate fi pus în evidență prin unda pe care acești ioni o formează în domeniul de potențial cuprins între 0 și —0,4 V față de electrodul de calomel saturat, în lipsa florurii de sodiu.

În tabelul 1 sînt redate rezultatele obținute la determinarea unor cantități de *o*-FDA. Se observă că eroarea relativă este de ±0,02%.

Tabelul 1

Rezultatele obținute la determinarea unor cantități de o-FDA

o-FDA luat mg/ml	*o*-FDA găsit mg/ml	Eroare relativă %
0,1296	0,1263	—0,02
0,1080	0,1105	+0,02
0,0864	0,0864	0,00
0,0648	0,0648	0,00
0,0432	0,0455	+0,01
0,0324	0,0324	0,00

3. Concluzii

Au fost stabilite condițiile determinării polarografice a *o*-FDA printr-o metodă indirectă bazată pe reducerea pe electrodul picător de mercur a 2,3-diaminofenazinei obținută prin oxidarea *o*-FDA cu ioni de Fe^{3+}. Reacția de oxidare decurge cantitativ la pH=2, iar unda polarografică este bine exprimată și proporțională cu concentrația soluțiilor de *o*-FDA la pH=6. Metoda propusă permite determinarea *o*-FDA cu o eroare relativă de ±0,02%.

Primită la 9 iulie 1980

Institutul politehnic, Iași,
Catedra de chimie fizică

BIBLIOGRAFIE

1. Parker E. R., Adams N. R., Anal. Chem., **28**, 823 (1956).
2. Elving J. P., Krivis F. A., Anal. Chem., **30**, 1645 (1958).
3. Lord S. S., Rogers B. L., Anal. Chem., **26**, 248 (1954).
4. Lee H. I., Adams R. N., Anal. Chem., **34**, 1587 (1962).

5. Ulman F., Manthmer F. Chem. Ber., **35**, 4302 (1902).
6. Mayer H., Berends N., Rec. Trav. Chem., **76**, 28 (1957).
7. Papafil M., Furnică M., An. Șt. Univ. „Al. I. Cuza", Iași, **VIII**, *1*, s. I, 191 (1962).
8. Furnică M., Bul. Inst. polit., Iași, **XXIV (XXVIII)**, *3—4*, s. II, 35 (1978).
9. Zuman P., *Organic Polarographie Analysis*. Prague, 1964, 83.
10. Furnică M., Bul. Inst. polit. Iași, **XXIV (XXVIII)**, *1—2* s. II, 35 (1978).

MÉTHODE POLAROGRAPHIQUE POUR LA DÉTERMINATION DE L'*o*-PHENYLÈNEDIAMINE

(Résumé)

On propose une méthode polarographique de détermination de l'*o*-PhDA, basée sur la réduction de la 2,3-diaminophenazine sur l'électrode à gouttes de mercure, obtenue par l'oxydation de l'*o*-PhDA avec les ions Fe^{3+} à pH=2. On fait réagir l'excès des ions Fe^{3+} avec NaF pour former des combinaisons complexes. Comme électrolyte indifférent on utilise le $NaNO_3$ et pour stabiliser le pH on utilise une solution tampon avec pH = 6. Après avoir éliminé l'oxygène de la solution étudiée on enregistre les courbes polarographiques dans le domaine de potentiel $-0,2 \ldots -0,8$ V par rapport à l'électrode de calomel saturé. La méthode permet la détermination de l'*o*-PhDA avec une erreur de $\pm$ 0,02%.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

C.Z. 669.75

ASPECTE CINETICE ALE ELECTRORAFINĂRII INTENSIVE A STIBIULUI ÎN MEDIU DE SbF_3 CU EXCES DE H_2SO_4 ŞI HF

DE

I. PÂRVU şi RADU VASILIU

1. Procesul de electrorafinare a stibiului, în condiţii clasice de electroliză, în regim static, decurge cu o viteză destul de redusă datorită procesului catodic care limitează viteza totală a procesului. Desigur, pentru scopuri industriale viteza procesului ar trebui să fie cît mai mare la o tensiune cît mai scăzută. Un asemenea rezultat se obţine folosind tehnica vibrării catodului, metodă introdusă în electrogravimetrie de către Gh. Facsko [1].

2. Comparînd metoda clasică statică, cu metoda vibrării catodului, aplicată în cazul electrorafinării stibiului în mediu de SbF_3 cu exces de H_2SO_4 şi HF, se constată următoarele :

Reprezentînd variaţia concentraţiei ionilor în funcţie de distanţa de la suprafaţa catodului, pentru regim static (fără vibrarea catodului) se obţine diagrama din fig. 1, în care C_r^s — concentraţia ionilor care se reduc la suprafaţa catodului ; C_r^v — concentraţia ionilor reductibili din volumul soluţiei ; δ_c — grosimea stratului de difuzie la catod.

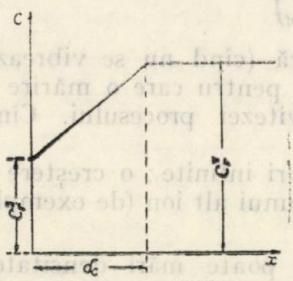


Fig. 1. — Schema variaţiei concentraţiei c a ionilor care se reduc, în funcţie de distanţa x de la suprafaţa catodului, pentru starea statică.

Cînd procesul catodic atinge echilibrul, viteza de difuzie, prin stratul δ_c, a ionilor care se reduc, va imprima viteza procesului catodic şi fiind stadiu limitativ, aceasta va fi însăşi viteza întregului proces [1], [2] :

$$i = \frac{nFD_r}{\delta_c}(C_r^v - C_r^s), \tag{1}$$

în care : n — numărul electronilor schimbaţi în procesul de electrod ; D_r — coeficientul de difuzie a ionilor care se reduc.

Potenţialul electrodului în absenţa curentului este :

$$\varepsilon_0 = \varepsilon^0 + \frac{RT}{nF}\ln C_r^v. \tag{2}$$

La trecerea curentului potenţialul devine :

$$\varepsilon_i = \varepsilon^0 + \frac{RT}{nF}\ln C_r^s. \tag{3}$$

Supratensiunea va fi dată de diferenţa celor două potenţiale :

$$\eta = \varepsilon_i - \varepsilon_0 = \frac{RT}{nF} \ln \frac{C_r^s}{C_r^v}. \tag{4}$$

Din relaţia (1) se determină concentraţia C_r^s în funcţie de densitatea de curent :

$$C_r^s = \frac{\frac{nFD_r}{\delta_c} C_r^v - i}{\frac{nFD_r}{\delta_c}}$$

şi se substituie în relaţia (4) de unde rezultă :

$$\eta = \frac{RT}{nF} \ln \frac{\frac{nFD_r}{\delta_c} C_r^v - i}{\frac{nFD_r}{\delta_c} C_r^v}, \tag{5}$$

care reprezintă expresia supratensiunii de transfer de masă în funcţie de concentraţia ionilor C_r^v. Dar

$$i_d = \frac{nFD_r}{\delta_c} C_r^v \tag{6}$$

reprezintă chiar curentul limită astfel că prin substituţie în relaţia (5) se obţine :

$$\eta = \frac{RT}{nF} \ln \frac{i_d - i}{i_d} = \frac{RT}{nF} \ln \left(1 - \frac{i}{i_d}\right). \tag{7}$$

Din relaţia (7) rezultă că pentru starea statică (cînd nu se vibrează catodul), viteza i poate creşte pînă la valoarea i_d pentru care o mărire a supratensiunii nu mai atrage nici o creştere a vitezei procesului. Cînd $i \to i_d$, $\eta \to -\infty$.

Supratensiunea nu ajunge în realitate la valori infinite ; o creştere a supratensiunii va atrage descărcarea pe electrod a unui alt ion (de exemplu hidrogen).

În consecinţă, pentru starea statică nu se poate mări densitatea de curent chiar dacă s-ar ridica tensiunea deoarece stadiul limitativ al procesului este independent de tensiune.

3. În cazul electrolizei stibiului, cînd nu se vibrează catodul, densitatea de curent catodic limită este de circa 150 A/m² [3]...[6] cu toate că densitatea de curent anodic limită poate avea valori în jur de 3 500 A/m² [7] ; electroliza va decurge cu densitatea de curent cea mai mică imprimată de stadiul limitativ.

În cazul catodului vibrator se produce o micşorare importantă a stratului de difuzie, δ_c, de la catod [8] ... [14], iar reprezentarea schematică

a variației concentrației ionilor care se reduc la catod, în funcție de distanța x de la suprafața catodului, capătă forma din fig. 2.

Prin micșorarea de cîteva ori a grosimii stratului, δ_c, rezultă din relația (6) o creștere a curentului i_d, ceea ce permite mărirea vitezei procesului pentru o supratensiune relativ scăzută. Aceasta înseamnă că pentru aceeași supratensiune aplicată în regim static se poate obține o densitate de curent mărită (în anumite limite) oferind practic posibilitatea intensificării procesului de electroliză.

Concluzia se confirmă în cazul determinărilor experimentale în mediu de SbF_3 cu exces de H_2SO_4 și HF folosind vibrarea catodului cu frecvența de 50 Hz și amplitudinea de 2 mm; în aceste condiții viteza liniară a electrodului este de ordinul 20 cm/s, mișcare care produce o rupere a stratului pelicular aderent la electrod.

Se ajunge la o intensificare a procesului de electroliză a stibiului, în condițiile amintite, de circa 20...25 ori față de metoda clasică, statică.

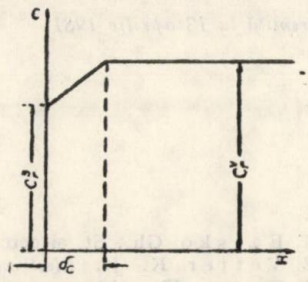


Fig. 2. — Schema variației concentrației c a ionilor care se reduc, în funcție de distanța x de la suprafața catodului, pentru starea în care se vibrează catodul cu frecvența de 50 Hz și amplitudinea de 2 mm.

Datele din tabelul 1 confirmă aceste rezultate pentru cazul electroliților cu 40 g/l HF, la diverse concentrații în H_2SO_4 și diferite conținuturi în Sb.

Tabelul 1

H_2SO_4 exces față de cantitatea stoechiometrică g/l	Conținut de Sb g/l	Densitatea de curent anodic limită A/m²	Densitatea de curent catodic limită A/m²	Domeniul densității de curent de lucru A/m²
25	5	2 600	2 200	2 200
	20	3 500	4 500	3 500
	40	4 200	5 000	4 000
50	5	2 400	2 200	2 200
	20	3 000	4 000	3 000
	40	3 600	6 000	3 600
	60	4 200	6 500	4 000
100	5	2 200	2 000	2 000
	20	2 600	4 000	2 600
	40	3 400	6 000	3 400
	60	3 600	6 500	3 600
300	5	2 200	2 000	2 000
	20	2 600	4 000	2 600
	40	3 400	6 000	3 400
	60	3 600	6 500	3 600

Astfel, pentru un electrolit cu 300 g/l H_2SO_4 (care este cel mai avantajos deoarece nu se depune Pb) și 40 g/l Sb, se constată, din tabelul 1, că densitatea de curent poate fi de 3 000 A/m², ceea ce reprezintă o valoare de 20 ori mai mare față de electroliza statică care funcționează la 150 A/m².

Primită la 13 aprilie 1981

Institutul politehnic „Tr. Vuia", Timișoara
și
Institutul politehnic, Iași,
Catedra de chimie fizică

BIBLIOGRAFIE

1. Facsko Gh., St. și cerc. șt., Timișoara **II**, *1—4*, 143—151 (1955).
2. Vetter K. J., *Electrochemical Kinetics*. Academic Press. N. Y., 1967.
3. Oprea Fl., Ilinescu E., Segărceanu T., Vișa L., *Metalurgia elementelor însoțitoare ale metalelor neferoase uzuale*. Ed. Tehn., București, 1968, 1—75.
4. * * * *Прикладная электрохимия*. Гл. **VII**, M., 1974, 110.
5. Eger G., *Handbuch der Technischen Elektrochemie*. Bd. **I**, Teil, Leipzig, 1961, 509—523.
6. Kupka Fr. Chemicky Primysl., **10/35**, *12*, 620—623 (1960).
7. Pârvu I., *Rafinarea electrolitică intensivă a stibiului*. Teză de doctorat, Inst. polit., Iași, 1979.
8. Facsko Gh., St. și cerc. șt., Chimie, Timișoara, **2**, 143 (1955).
9. Facsko., Gh., Rădoi I., St. și cerc. șt., Chimie, Timișoara, **4**, 107 (1957).
10. Facsko Gh., St. și cerc. șt., Chimie, Timișoara, **4**, 91 (1957).
11. Facsko Gh., Rădoi I., St. și cerc. șt., Chimie, Timișoara, **8**, 265 (1961).
12. Facsko Gh., Rădoi I., Acta Chim. Acad. Sci. Hung., **27**, 31 (1961).
13. Facsko Gh., Rădoi I., Golumbiovschi Fr., St. și cerc. șt., Chimie, Timișoara, **7**, 45 (1962).
14. Facsko Gh., Rev. Roumaine de Chimie, **11**, *2*, 191—205 (1966).

KINETIC ASPECTS OF INTENSIVE ELECTROREFINING OF ANTIMONY IN A SbF_3 MEDIUM WITH H_2SO_4 AND HF IN EXCESS

(Summary)

The kinetics of the antimony electrorefining process and the possibilities for intensification of the electrolysis are studied. The obtained experimental results during the electrorefining of antimony with a vibrating cathod at a 50 Hz frequency and 2 mm amplitude, in an SbF_3 medium with H_2SO_4 and HF in excess confirmed the expectation concerning the intensification of the cathodic deposition within the experimental procedure proposed by the authors. For the above reported case, the intensification of the electrolysis process was approximately 20...25 times higher as compared to the deposition of antimony using a classical method.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

D.C. 547-931 ; 66.062

WATER REMOVAL FROM SOME ORGANIC SOLVENTS ON VOLCANIC TUFFS

BY

P. ONU, GH. MIHĂILĂ, N. BÎLBĂ, C. LUCA and D. GÎNJU

1. Introduction

The volcanic tuffs are natural raw materials found in large deposits. Due to their structural adsorptive properties, they present many possibilities of utilization for different industrial purposes. As a result of the investigations performed in this field, the volcanic tuffs become employed in various domains such as: binder, glass and ceramics industry, agriculture, catle and chiken farms, gas separation, etc. [1].

This paper deals with a study regarding the possibility of volcanic tuff from Mîrşid deposit, Romania, to be utilized for water removal from some organic solvents such as: methylic alcohol, ethylic alcohol, propylic alcohol, benzene, methylethylketone and dimethylketone. Selection of this tuff was done on the basis of a deep experimental investigation [2] that indicated a more BET - specific surface area, a high content of clinoptilolite, the presence of micropores with their cross section close to that of water molecules and its adsorption capacity against water of 11.0...13.0%.

2. Experimental

The experiments have been carried out on volcanic tuffs samples, having granula of size 0.5...2.0 mm. In order to improve its adsorptive properties, the tuff was activated thermically in air stream, at an optimum temperature, determined on experimental way. There were studied three types of samples: native tuff, water washed tuff and 2% HCl solution treated tuff. The determinations regarding their anhydrization capacity were carried out under dynamic conditions, using a laboratory plant with a packing capacity of 1 000 g tuff, represented in Fig. 1.

2.1. Preparation of the Samples

The samples to be tested were activated thermically, chemically and by water washing.

The thermal activation was carried out *in situ* using 1 000 g tuff each time. In order to establish the optimal conditions for thermal activation, the tuff samples were heated for two hours at the temperatures of 200°, 250°, 300° and 400°C. Activation was done in dry air stream of

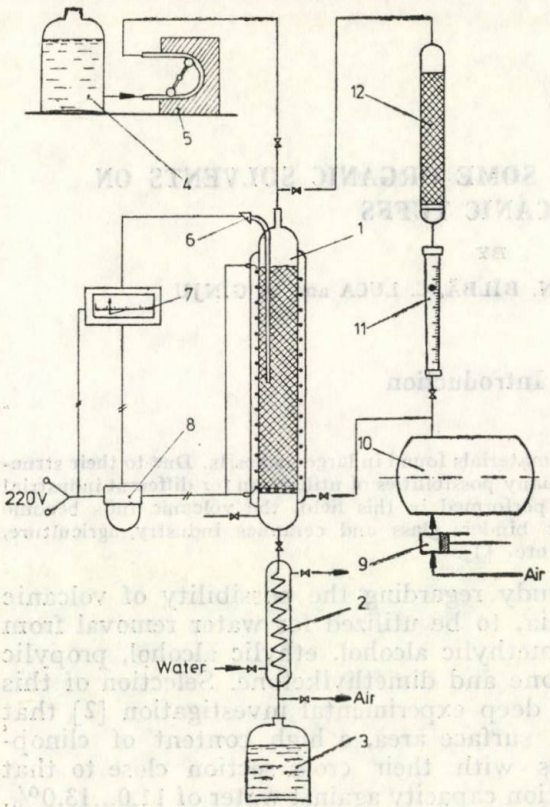


Fig. 1. — Laboratory plant for water removal from organic solvents on volcanic tuffs: *1* — packed bed adsorption column; *2* — cooler; *3* — anhydrous solvent receiver; *4* — solvent — water vessel; *5* — peristaltic pump; *6* — thermocouple; *7* — temperature controller; *8* — tension oil switch; *9* — air compressor; *10* — pressured air receiver; *11* — flowmeter; *12* — packed bed drying column.

20 cm³/min. To determine which of the samples exhibit a greater adsorption capacity against water, the same amount of ethylic alcohol with 5.5% water was passed over the activated and cooled tuff samples. The obtained results are represented in Fig. 2.

As it can be seen in Fig. 2, the greater activation temperature, the greater adsorption capacity against water. The samples activated at 300° and 400°C having a close behaviour, from economical view point, the temperature of 300°C was selected as being optimum one.

Taking into account that volcanic tuff to be tested has a high content of clinoptilolite, the activation temperature of 300°C is comparable to that found in literature [3], [4].

To avoid the rapid evaporation of water and solvent, phenomenon which can create tensions inside the granules leading to their mechanical resistance diminishing, the heating rate during activation was not over 2 ... 3°C/min.

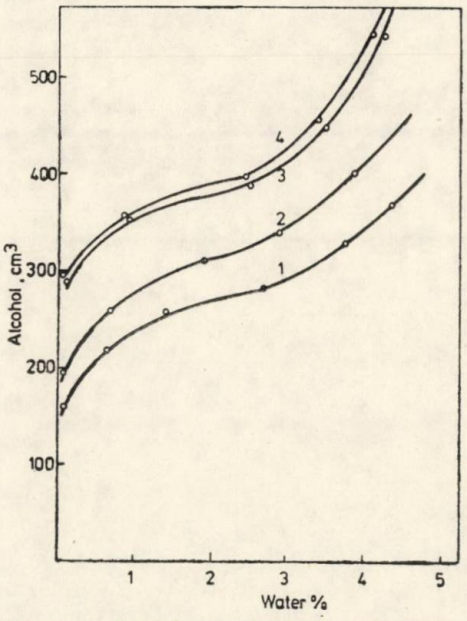


Fig. 2. — Variation of water concentration in the alcohol passed through volcanic tuff bed activated at different temperatures: 1 — 200°C; 2 — 250°C; 3 — 300°C; 4 — 400°C.

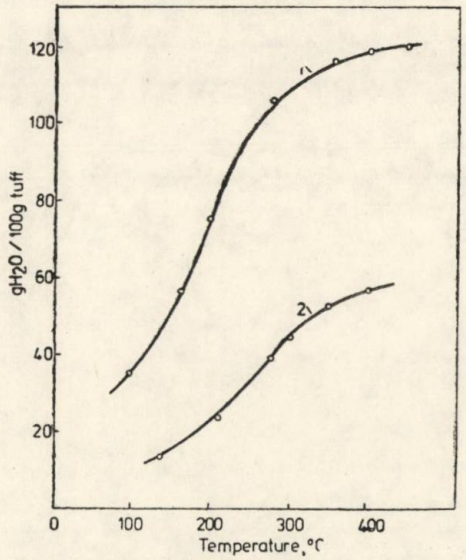


Fig. 3. — Water loss against temperature at steady state: *1* — native tuff; *2* — tuff treated with 2% HCl solution.

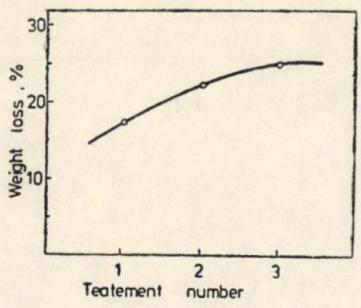


Fig. 4 — Weight loss of the tuff treated successively with 2% CH1 solution.

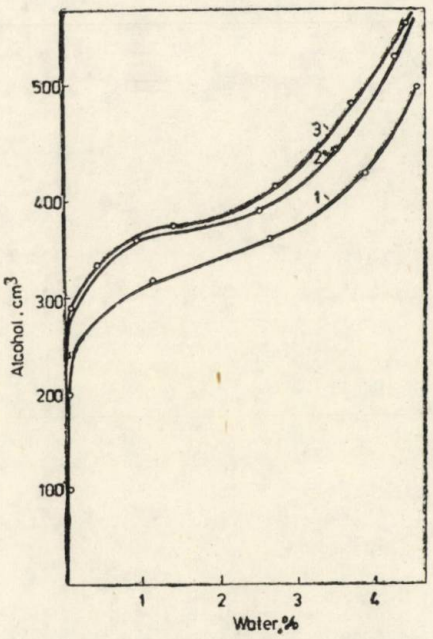
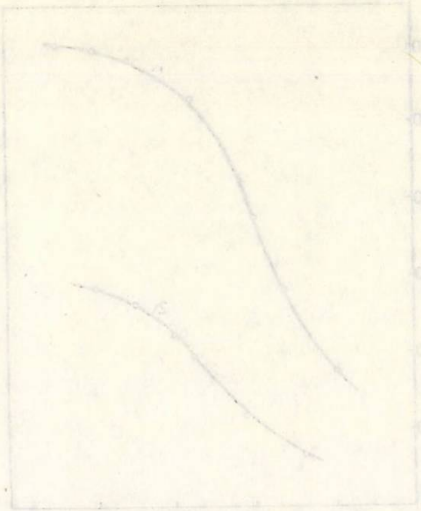
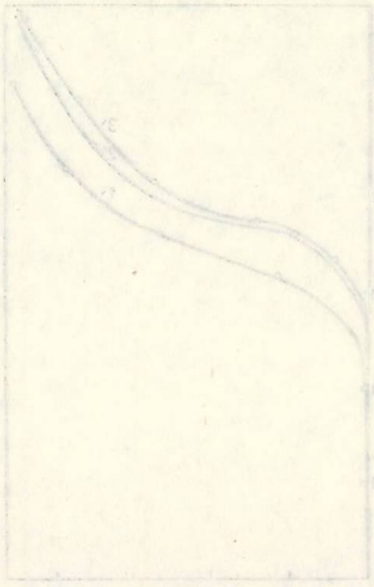


Fig. 5 — Water adsorption from the ethylic alcohol — water system on different samples of tuff: *1* — nontreated tuff; *2* — treated with 2% HCl solution; *3* — washed with water.





By thermal activation one follows to increase the specific surface area of the samples and adsorption capacity, respectively. This increase was realized by volatile components removal, especially water. Looking over the curves plotted in Fig. 3, there is a difference in the behaviour of native tuff and acid treated tuff as regards their water loss against temperature, determined at steady state.

Water loss of the acid treated tuff is less, because during acid treatment a part of the microporous structure was destroyed by dissolving of some soluble components. The micropores become larger in their cross section and due to this reason their adsorption capacity become less.

The chemical activation was carried out by treating the samples with low concentration hydrochloric acid solution. The previous results shown that the best adsorption capacity exhibit the samples treated with 2% HCl solution [2]. In this paper one studied the influence of successive acid treatment of the sample. For this reason, a tuff sample was treated in several steps with 2% HCl solution, using a mixing ratio of 200 cm^3 solution to 100 g tuff. The acid treatment was done for two hours at 100°C. On this way one studied also the weight loss of sample for each step of acid treatment as well as the optimal number of steps (Fig. 4). The highest weight loss is obtained during the first step of acid treatment (17.5%), in the second step the weight loss is 5% and in the third step this is only 3%. To know the adsorption properties of these samples, they were activated

Table 1

Statical Adsorption of Water

Sample	Non-treated tuff	Acid treated tuff in three steps		
		1	2	3
Adsorpted water %	12.2	14.1	14.6	14.5

thermically for two hours at 200°C. On these samples was performed statical adsorption of water for 24 h. The obtained results, comparatively to those given by the nontreated tuff, activated under the same conditions, are summarized in Table 1.

As it comes out from Table 1, there is a difference of 1.9% between the sample treated one time and that nontreated and, the samples treated from one to three steps exhibit close adsorption capacity, consequently, more economic is acid treatment of the samples only one step.

Activation of the samples by water treatment was performed *in situ* too. The 1 000 g tuff sample packed in the column was washed continuously in descendent stream with 4 l distilled water, under a flowrate of 10...14 cm^3/min. The washings are opalescent and weak yellow in colour, and after 15 ... 20 min., a layer of very fine particles are setlled. Practically, one observed that washing must be not longer than 30 ... 50 min., because

there takes place a goffering process in tuff granules that determines a gradual diminishing of their mechanical resistance. After thermal activation, the samples of tuff washed with water exhibited an adsorption capacity comparable to those acid treated (Fig. 5).

3. Results and Discussion

3.1. Water Removal from Alcohols

The experiments were performed in order to remove water from methylic, ethylic and propylic alcohol. Of great interest is anydrization of ethylic alcohol which forms an azeotropic mixture of 99.57% alcohol and 4.43% water [5]. Obtention of the absolute ethylic alcohol can be carried out by different procedures, the most utilized being azeotrope distillation with benzene or sulfuric acid.

The behaviour of the three alcohols on volcanic tuff was similar, the practical results showing the same final concentration for all of them. Their anhydrization was done at 25°C. The ethylic and the methylic alcohol to be anhydrized have had initial concentration of 5.5% water and the propylic alcohol, 2% water, being less soluble in it.

The best behaviour, as anhydrization agent, had the tuff washed with water, and the worst that nontreated one (Fig. 5). The tuff washed with 2% HCl solution has an intermediary adsorption capacity, but very close to that of the water washed tuff. In all cases, alcohol was not anhydrized completly, its remanent water concentration being of 0.1 ... 0.2%. Even the alcohol with this low water content was passed again on activated tuff, its water content remained the same.

The amount of alcohol with 0.1 ... 0.2% water obtained on the three types of tuff samples was 230 ... 240, 250 ... 260 and 260 ... 275 cm^3/Kg, respectively. Since the initial content of water in propylic alcohol was less, the amount of anhydrized product was about 2.3 ... 2.4 times greater.

In all cases, the anhydrized alcohol, indifferent by its water content, has an yellow colour and is opalescent. After a while, an white yellow layer of very fine particles are setlled. This fact points out that during activation and especially during anhydrization, the cohesion of granules in tuff becomes lower and consequently, they can be carried away by the descendent solvent stream.

The volcanic tuff contains an appreciable number of components, each of them having a certain dilatation coefficient, during activation inside of granules occur internal tensions which gradually lead to their grinding. The colour and opalescence of anhydrous alcohol is due to the presence of these fine particles and inorganic and organic compounds extracted from the mass of tuff sample.

To verify the purity of the alcohols anhydrized on volcanic tuff, they were analyzed flamphotometrically, determining their sodium content (Table 2).

Table 2

Sodium Content, [mg Na. $10^3/cm^3$] *in the Anhydrized Alcohol*

Operating time min.	Native tuff	Water washed tuff	Tuff treated with 2% HCl solution
5	2 100	300	400
10	800	350	300
15	2 000	180	300
20	7 000	180	300
25	7 600	180	290
30	7 600	180	200
35	5 500	180	250
40	2 100	170	230
45	1 800	160	200

The data summarized in Table 2 are referring to the concentration of natrium in the alcohol passed only one time over the activated tuff. All tuff samples, indifferent of their activations and anhydrizations number, transfer to the alcohol an appreciable amount of natrium cations and less potassium cations. Little amounts of calcium and magnesium were detected flamphotometrically too.

In order to determine the influence of temperature on adsorption capacity of tuff, anhydrization was carried out at different temperatures (Fig. 6).

As it comes out from Fig. 6, the lower temperature the higher adsorption capacity and the utilization degree of the tuff is better.

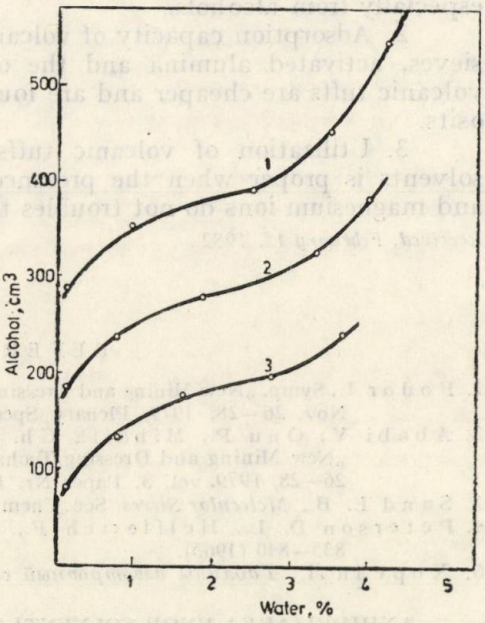


Fig. 6. – Temperature influence on adsorption capacity of volcanic tuff against water: *1* – 250°C; *2* – 45°C; *3* – 85°C.

3.2. Anhydrization of Benzene, Methylethylketone and Dimethylketone

The compounds mentioned above, especially benzene, have various practical uses, e.g., benzene is utilized for obtention of cyclohexanol, caprolactum, ethylbenzene, styrene, α-methyl-styrene, etc. Almost all their chemical transformations being catalytical processes, they must be performed in the absence of water.

Anhydrization capacity of volcanic tuff is enough to diminish the water amount as much as necessary in industrial practice. Being solvent better than the alcohols, methylethylketone, dimethylketone and especially benzene, anhydrizated on volcanic tuff, they become more intensive yellow coloured. Also, these solvents extract an appreciable amount of sodium, potassium, calcium and magnezium (Table 3).

Table 3

Sodium Content, [mg Na.10^3/cm^3], *in Different Solvents Anhydrized on Water Washed Volcanic Tuff*

Operating time min.	Solvent		
	Benzene	Methylethylketone	Dimethylketone
5	250	1 000	1 800
10	220	1 100	1 800
15	263	1 180	1 600
20	270	1 200	1 700
25	240	1 150	1 650
30	225	1 110	1 700
35	195	1 125	1 675
40	180	1 100	1 650

4. Conclusions

From the experimental results presented above, the following conclusions may be drawn :

1. The volcanic tuff, having an appreciable adsorption capacity against water, can be employed successfully for water removal from many solvents, especially from alcohols.

2. Adsorption capacity of volcanic tuffs is less than that of molecular sieves, activated alumina and the other industrial adsorbents, but the volcanic tuffs are cheaper and are found in great amounts in natural deposits.

3. Utilization of volcanic tuffs for water removal from different solvents is proper when the presence of the sodium, potassium, calcium and magnesium ions do not troubles the next technological steps.

Received, February 15, 1982

Polytechnic Institute, Jassy. Department of General Chemistry and Chemical Technology

REFERENCES

1. Fodor I., Symp. „New Mining and Dressing Technologies of Non-metallics", Cluj-Napoca, Nov. 26—28, 1979, Plenary Speech.
2. Ababi V., Onu P., Mihăilă Gh. ,Bîlbă N., Luca C., Naum N., Symp. „New Mining and Dressing Technologies of Non-metallics", Cluj-Napoca, Nov. 26—28, 1979. vol. 3, Paper Nr. *12*.
3. Sand L. B., *Molecular Sieves*. Soc. Chem. Ind., London, 1968, 71.
4. Peterson D. L., Helfferich F., Blytas G. C., Phys. Chem. Solids, **26**, 835—840 (1965).
5. Хорсли Л., *Таблицы азеотропный смесей* (пер. с англ.). ИИЛ, М., 1951, 29.

ANHIDRIZAREA UNOR SOLVENŢI ORGANICI PE TUFURI VULCANICE

(Rezumat)

S-au studiat condiţiile de anhidrizare a primilor trei alcooli din seria alifatică, a benzenului, a metiletilcetonei şi a dimetilcetonei pe tuf vulcanic de Mirşid, România, activat termic şi chimic. Activarea şi anhidrizarea s-au efectuat într-o coloană cu strat fix, cu 1 000 g tuf. Realizîndu-se anhidrizări ale alcoolului etilic pe tuf vulcanic activat la diferite temperaturi, s-a găsit că temperatura optimă de activare este de 300°C. Tuful vulcanic, avînd o capacitate de absorbţie apreciabilă faţă de apă, conduce la o anhidrizare a alcoolilor pînă la 0,1...0,2%, dar impurifică solvenţii cu cantităţi diferite de ioni de sodiu, potasiu, calciu şi magneziu şi cu particule foarte fine de tuf.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

D.C. 66.097.7 ; 669,1 ; 669.26 ; 669.5

SEPARATION OF IRON, CHROME AND ZINC FROM A WASTE OXIDIC CATALYST

BY

ANGELA POPA, ANIŞOARA BOLD, GH. MIHĂILĂ, M. CRUCEANU and EVELINE POPOVICI

1. Introduction

Characterization of any catalyst is made by means of chemical composition, catalytic activity, physical properties and mechanical strength. These characteristics have well precised values for a new catalyst and are modified continuously during exploitation, becaming, after a certain time, improper to the process. Therefore, after a certain number of cyclic regenerations, most of them undergo some irreversible transformations and require to be replaced. The main industrial chemical processes using, particularly, catalysts on the basis of metallic oxides with or without inert carrier, difficult to be regenerated, lead to great amounts of such waste catalysts, whose revaluation has become a real problem.

In the last two decades, amount of waste catalysts increased very much in all developed countries and, consequently, there are developing programmes as regards both separation of the catalytic active metalls [1]...[3] and inert carrier [4]. Since degradation of the catalysts is a complex process, the revaluation ways are proper to each of them [5], [6].

The present paper deals with the results obtained on investigation, at laboratory scale, of the iron, chrome and zinc separation from a waste catalyst employed for hydrocarbons dehydrogenation in gaseous phase, by acid dissolution of metallic oxides, followed by ion exchange separation of the components from extract.

2. Experimental

The industrial waste catalyst is in fact a mixture of dehydrogenation catalysts ; it contains 48...50% Cr_2O_3, 24...26% Fe_2O_3 and 22...23% ZnO. It is made up by cylindrical granules with poor mechanical strength in mixture with powder, both dark red in colour. After fine grinding in ball mill pulverizer, catalyst was sizing in six granulometric fractions with the diameter ranging between 0.01 and 0.5 mm. Dissolution of the metallic oxides was carried out with solution of HCl, H_2SO_4 and HNO_3 at different ratios liquid to solid against time and temperature. Extraction operation was realized under stirring and quantitative determination of the extracted components was performed using atomic absorption spectroscopy on apparatus UNICAM SP-90 A. Separation of the metallic ions was made by ion exchange chromatography, using as stationary phase an ion exchanger in H^+ form, Vionit CS-2, supplied by Chemical Works „Victoria", Victoriatown, Romania.

3. Results and Discussion

The quantitative appreciation of the extraction was made by means of extraction degree η, defined as percent ratio of the amount of extracted

metal and total amount of it in the initial sample. Composition of the solvent was expressed volumetrically, i.e., numbers of the concentrated solution volumes (37.7% HCl, 98% H_2SO_4 and 42% HNO_3) in 100 volumes of aqueous solvent for extraction. After finding the optimum ratio liquid to solid (L/S), namely 50, each granulometric fraction was treated with hydrochloric solution, under stirring, at room temperature, for one hour. By comparison of the obtained results it was established that utilization of the granule size with mean diameter less than 0.10...0.15 is not indicated because below this value, diameter diminishing is not followed by an appreciable increasing of the extraction degree.

In order to select the most suitable acid and its optimum concentration, several extractions have been carried out under standardized conditions. The extraction with hydrochloric acid at 21°C for a hour, (Fig. 1), shows that the extraction degree of iron is of 2...3 times greater than that of chrome and zinc. At the same time, it can be seen that utilization for extraction of some solutions with a content of concentrated acid larger then 60% is not justified because it does not cause a corresponding increase of the extraction degree.

Making similar plots also in the case of extraction with H_2SO_4 and HNO_3, the optimum concentrations of these acids has been established, i.e., 70% water and 30% concentrate solution of H_2SO_4 and 80% water and 20% concentrate solution of HNO_3. For the solvents with such determined concentration, influence of temperature over the extraction degree of the three ions, using the same ratio liquid to solid, the same granule size for the same contact time, has been investigated. The results obtained in the case of extraction with hydrochloric acid are represented in Fig. 2.

As it comes out from Fig. 2, extraction of iron depends strongly on temperature ($\Delta\eta/\Delta t=0.4...0.7$) while extraction of chrome and zinc is less influenced by this parameter ($\Delta\eta/\Delta t=0.04...0.15$).

The results presented in Fig. 2 allowed to select the temperature of 75°C for further investigation, namely dependence of the three ions extraction on the nature of employed mineral acid. The results obtained are set out in Figs. 3...5. The obtaind results show that the extraction capacity of the three mineral acids are situated in the order :

$$H_2SO_4 > HCl > HNO_3$$

and the extraction degree of the three ions are situated as below :

$$\text{Iron} > \text{Zinc} > \text{Chrome}.$$

In order to increase the amount of extracted ions, five repeated extractions on the same waste catalyst sample, at 75°C, for one hour each, using the ratio liquid to solid equal to 50, have been carried out. The obtained results are summarized in Table 1. The data from these table show a substantial increase of the total extraction degree for each of the three ions against the extraction number, but performing a number of extraction greater than 3 or 4 is not justified by an appreciable increase of the extraction degree.

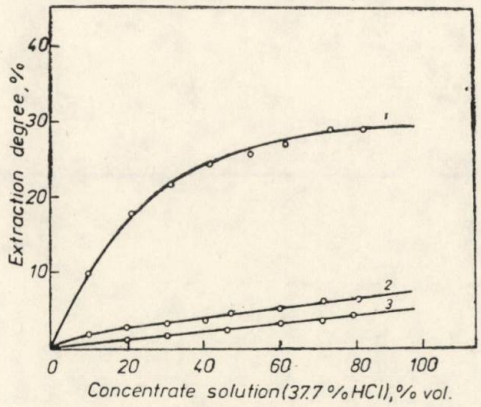


Fig. 1. — Dependence of the extraction degree of the three ions on solvent concentration: *1* — Fe^{3+}; *2* — Cr^{3+}; *3* — Zn^{2+}.

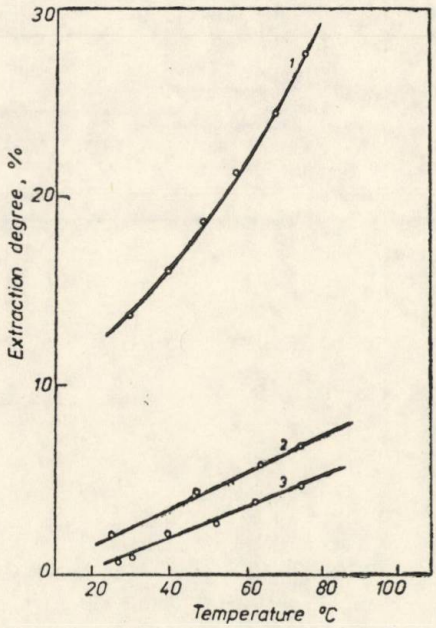


Fig. 2. — Extraction of the three ions with hydrochloric solution vs. temperature: *1* — Fe^{3+}; *2* — Cr^{3+}; *3* — Zn^{2+}.

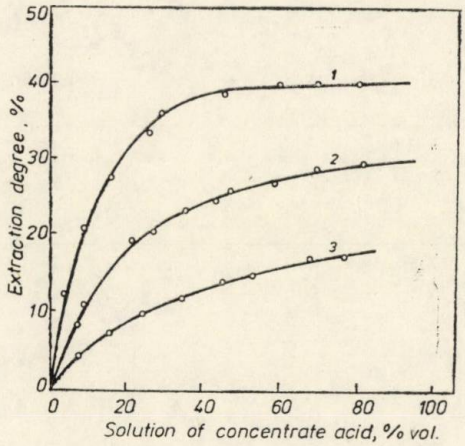


Fig. 3. — Dependence of the extraction degree of iron vs. the nature of employed acid: *1* — H_2SO_4; *2* — HCl; *3* — HNO_3.

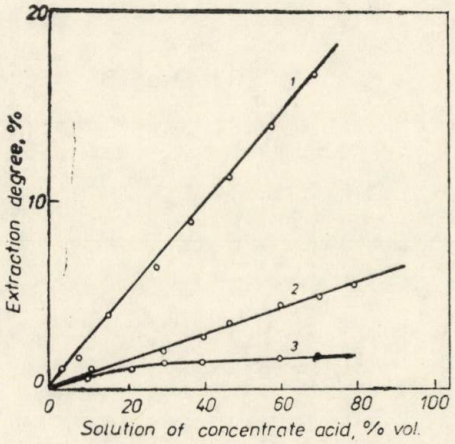
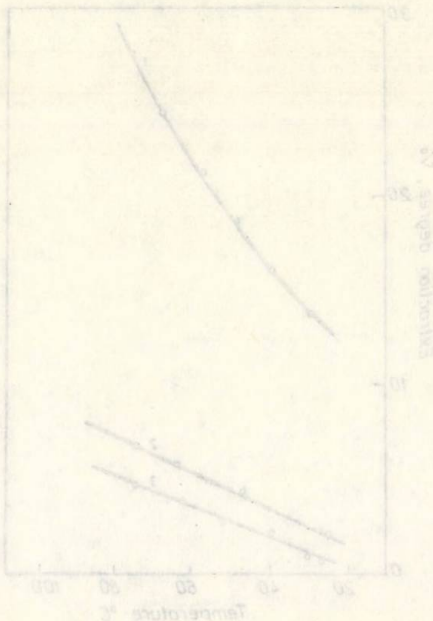


Fig. 4. — Dependence of the extraction degree of chrome vs. the nature of employed acid: *1* — H_2SO_4; *2* — HCl; *3* — HNO_3.



Separation of the three ions from acid extract has been carried out by ion exchange chromatography. Preceding selectivity test of the ion exchanger „Vionit CS-2" against these ions pointed out that iron is retained entirely, chrome 75% and zinc 94.3%. Elution with hydrochloric acid solution of different concentration indicated that utilization of 0.1 N solution of HCl, Fe^{3+} and Zn^{2+} are removed, while Cr^{3+} is still retained; it can be removed then by elution with 1 N solution of HCl. Further on, separation from one another of the Fe^{3+} and Zn^{2+} can be realized with a mixture of 0.64 N solution of HCl — acetone with 80% acetone and with 37% acetone for Fe^{3+} and Zn^{2+}, respectively.

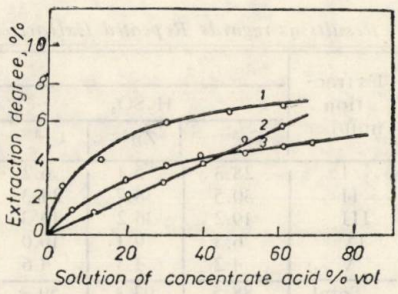


Fig. 5. — Dependence of the extraction degree of zinc vs. the nature of employed acid: *1* — H_2SO_4; *2* — HCl; *3* — HNO_3.

On the basis of the obtained results regarding both extraction and separation by ion exchange, a flow diagram of the process for the three ions separation from waste catalyst was set out in Fig. 6.

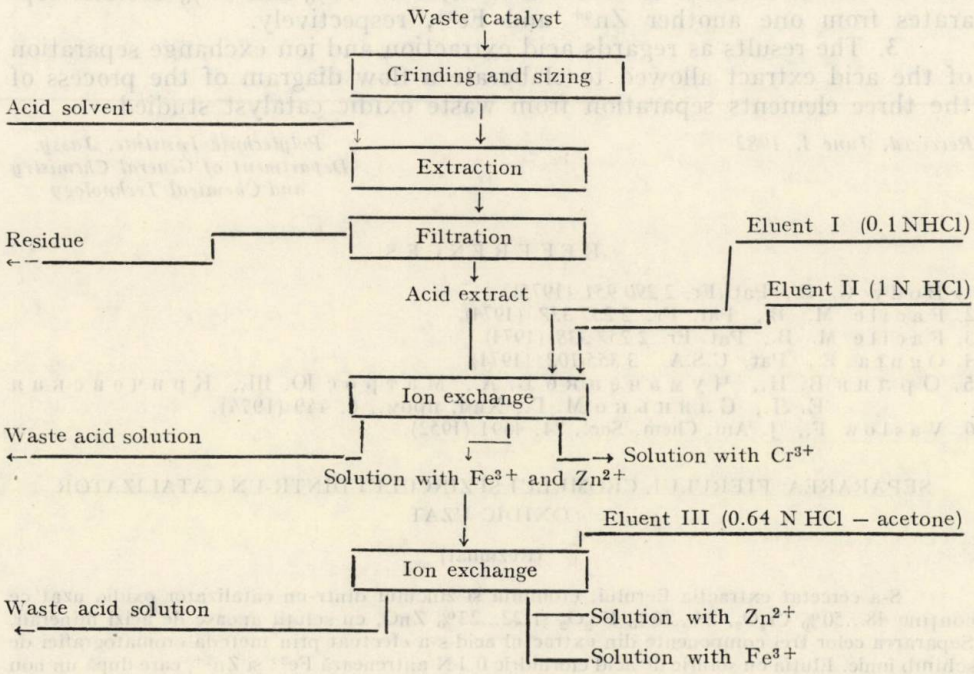


Fig. 6. — Flow diagram of the process for the Fe^{3+}, Cr^{3+} and Zn^{2} ions separation from a waste oxidic catalyst.

Table 1

Results as regards Repeated Extraction of Iron, Zinc and Chrome with three Mineral Acids

Extraction number	Aqueous solution of :								
	H_2SO_4			HCl			HNO_3		
	Fe^{3+}	Zn^{2+}	Cr^{3+}	Fe^{3+}	Zn^{2+}	Cr^{3+}	Fe^{3+}	Zn^{2+}	Cr^{3+}
I	28.3	5.1	6.2	27.0	4.3	5.7	20.1	3.2	4.3
II	30.5	38.7	24.3	31.2	43.7	23.4	30.2	40.1	19.2
III	19.2	36.2	14.3	16.0	31.0	13.0	17.5	25.2	12.8
IV	6.3	9.1	10.0	5.3	8.7	9.2	4.6	9.8	7.3
V	4.2	4.3	4.6	1.2	3.2	3.4	8.3	4.7	1.5
Total	88.5	93.4	59.4	80.7	90.9	54.7	80.7	83.0	45.1

4. Conclusions

1. The conditions of acid dissolution with aqueous mineral acid solution of iron, chrome and zinc from a mixture of waste catalysts that contains 48...50% Cr_2O_3, 24...26% Fe_2O_3 and 22...23% ZnO, have been investigated.

2. Separation of the three ions from the acid extract has been done by ion exchange chromatography. Elution with 0.1 N solution of HCl removes the Fe^{3+} and Zn^{2+} ions, while elution with 1.0 N solution of HCl, removes the Cr^{3+} ions. A new ion exhange followed by elution with a mixture of 0.64 N solution of HCl — acetone, with 80% and 57% acetone separates from one another Zn^{3+} and Fe^{3+}, respectively.

3. The results as regards acid extraction and ion exchange separation of the acid extract allowed to elaborate a flow diagram of the process of the three elements separation from waste oxidic catalyst studied.

Received, June 1, 1982

Polytechnic Institute, Jassy,
Department of General Chemistry
and Chemical Technology

REFERENCES

1. Body G. E., Pat. Fr. *2 290 951* (1975).
2. Facile M. B., Pat. Fr. *2 257 337* (1974).
3. Facile M. B., Pat. Fr. *2 257 338* (1974).
4. Ogura E., Pat. U.S.A. *3 355 102* (1971).
5. Орлик В. Н., Чумаченко В. А., Матрос Ю. Ш., Кричевская Е. Л., Слинько М. Г., Хим. пром., *6*, 449 (1974).
6. Vaslow F., J. Am. Chem. Soc., **74**, 4691 (1952).

SEPARAREA FIERULUI, CROMULUI ŞI ZINCULUI DINTR-UN CATALIZATOR OXIDIC UZAT

(Rezumat)

S-a cercetat extracţia fierului, cromului şi zincului dintr-un catalizator oxidic uzat ce conţine 48...50% Cr_2O_3, 24...26% Fe_2O_3 şi 22...23% ZnO, cu soluţii apoase de acizi minerali. Separarea celor trei componente din extractul acid s-a efectuat prin metoda cromatografiei de schimb ionic. Eluţia cu soluţie de acid clorhidric 0.1 N antrenează Fe^{3+} şi Zn^{2+}, care după un nou schimb ionic se separă prin eluţie cu un amestec format din acetonă şi soluţie de acid clorhidric 0,64 N, cu 80% acetonă pentru Zn^{2+} şi cu 57% acetonă pentru Fe^{3+}. Pe baza rezultatelor obţinute s-a elaborat fluxul tehnologic al procesului de separare a celor trei elemente din catalizatorul oxidic uzat, la scară de laborator.

Table 1

Results as regards Repeated Extraction of Iron, Zinc and Chrome with three Mineral Acids

Extraction number	Aqueous solution of :								
	H_2SO_4			HCl			HNO_3		
	Fe^{3+}	Zn^{2+}	Cr^{3+}	Fe^{3+}	Zn^{2+}	Cr^{3+}	Fe^{3+}	Zn^{2+}	Cr^{3+}
I	28.3	5.1	6.2	27.0	4.3	5.7	20.1	3.2	4.3
II	30.5	38.7	24.3	31.2	43.7	23.4	30.2	40.1	19.2
III	19.2	36.2	14.3	16.0	31.0	13.0	17.5	25.2	12.8
IV	6.3	9.1	10.0	5.3	8.7	9.2	4.6	9.8	7.3
V	4.2	4.3	4.6	1.2	3.2	3.4	8.3	4.7	1.5
Total	88.5	93.4	59.4	80.7	90.9	54.7	80.7	83.0	45.1

4. Conclusions

1. The conditions of acid dissolution with aqueous mineral acid solution of iron, chrome and zinc from a mixture of waste catalysts that contains 48...50% Cr_2O_3, 24...26% Fe_2O_3 and 22...23% ZnO, have been investigated.

2. Separation of the three ions from the acid extract has been done by ion exchange chromatography. Elution with 0.1 N solution of HCl removes the Fe^{3+} and Zn^{2+} ions, while elution with 1.0 N solution of HCl, removes the Cr^{3+} ions. A new ion exhange followed by elution with a mixture of 0.64 N solution of HCl — acetone, with 80% and 57% acetone separates from one another Zn^{3+} and Fe^{3+}, respectively.

3. The results as regards acid extraction and ion exchange separation of the acid extract allowed to elaborate a flow diagram of the process of the three elements separation from waste oxidic catalyst studied.

Received, June 1, 1982

Polytechnic Institute, Jassy,
Department of General Chemistry
and Chemical Technology

REFERENCES

1. Body G. E., Pat. Fr. *2 290 951* (1975).
2. Facile M. B., Pat. Fr. *2 257 337* (1974).
3. Facile M. B., Pat. Fr. *2 257 338* (1974).
4. Ogura E., Pat. U.S.A. *3 355 102* (1971).
5. Орлик В. Н., Чумаченко В. А., Матрос Ю. Ш., Кричевская Е. Л., Слинько М. Г., Хим. пром., *6*, 449 (1974).
6. Vaslow F., J. Am. Chem. Soc., **74**, 4691 (1952).

SEPARAREA FIERULUI, CROMULUI ŞI ZINCULUI DINTR-UN CATALIZATOR OXIDIC UZAT

(Rezumat)

S-a cercetat extracţia fierului, cromului şi zincului dintr-un catalizator oxidic uzat ce conţine 48...50% Cr_2O_3, 24...26% Fe_2O_3 şi 22...23% ZnO, cu soluţii apoase de acizi minerali. Separarea celor trei componente din extractul acid s-a efectuat prin metoda cromatografiei de schimb ionic. Eluţia cu soluţie de acid clorhidric 0.1 N antrenează Fe^{3+} şi Zn^{2+}, care după un nou schimb ionic se separă prin eluţie cu un amestec format din acetonă şi soluţie de acid clorhidric 0,64 N, cu 80% acetonă pentru Zn^{2+} şi cu 57% acetonă pentru Fe^{3+}. Pe baza rezultatelor obţinute s-a elaborat fluxul tehnologic al procesului de separare a celor trei elemente din catalizatorul oxidic uzat, la scară de laborator.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

D.C. 661.846.22

CHEMICAL ENGINEERING RESEARCHES ON THE PROCESS OF $Mg(OH)_2$ PREPARATION

II. RESEARCH ON THE SPECIFIC INFLUENCE OF SOME KINETIC FACTORS OVER THE OBTAINED PRODUCT CHARACTERISTICS

BY

LIVIA IFRIM, CORNELIA LEONTE, Al. SZÉP and C. CALISTRU

1. Introduction

Within a previous work [1] the process of $Mg(OH)_2$ preparation on the basis of a technological scheme inside the ammoniacal soda industry, was analysed. The aspects concerning the industrial stoichiometry of the process were discussed, as well as those corresponding to the possible macrokinetic mechanisms and models for the process development. Under those circumstances the fact was underlined that, from the two possible mechanisms for the process developing, the process of $Mg(OH)_2$ precipitation must follow — for its achievement on an industrial scale, the mechanism : $Ca(OH)_2$ dissolving — chemical reaction — $Mg(OH)_2$ germs formation and growth in order to assure an as advanced as possible $Ca(OH)_2$ transformation and a corresponding advanced purity of the final product. Within this macrokinetic mechanism the most important part is played by the complex process of the new phase germs formation (nucleation) and growth, this depending closely on the imposed qualities of the $Mg(OH)_2$ precipitate.

2. Theoretical Considerations

The numerous works consacrated to this process and published in the literature [1]...[7] hasn't yet permited the elaboration of an unitarian theory to lead toward the preparation of a product with imposed characteristics. Under normal precipitation conditions, $Mg(OH)_2$ is strongly floculated, has a semicolloidal structure and shows a relatively slow settling and filtration rates [2], [6]. The preparation of such a product is determined by the instant formation of a very great number of the nuclei in the moment of the reactant phases contactation.

In order to eliminate this phenomenon, it is necessary to know and to act by means of all the factors having a significant influence durring the complex process of the new phase germs formation and growth.

We include among them — as in this field literature shows [2], [8] : the work temperature, the way of addition and the amount of reactants, the intensity of phases mixing and the presence of „initiators" crystals inside the reaction mass.

With the nowadays theory of the crystalization process, the overall process of the new solid phase preparation can follow the schema (Figs. 1 and 2) [9] :

Reactant phases contact ——1——→ The end of the reaction ——2——→ The beginning of the new phase separation ——3——→ The end of the new phase separation.

Fig. 1.—Process development in three steps.

In accordance with the schema from Fig. 1, the process of the new phase separation includes the following steps : supersaturation, induction and disappearance of supersaturation (nucleation).

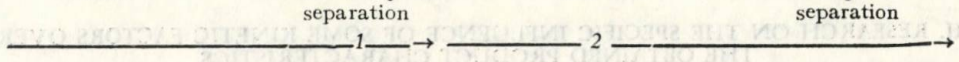


Fig. 2. — The development of the two stages process.

It is possible that the process of the formation and growth of nuclei develops within the mechanism with two steps (Fig. 2). In these conditions the beginning of the new phase separation takes place before the end of the chemical reaction. The first step is the one of the formation of supersaturation ; in the second step take place the disappearance of the supersaturation.

The development of the $Mg(OH)_2$ preparation process following one of the already mentioned schemes, will be determined by the real conditions for its achievement, conditions leading to a product with specific characteristics. Within each scheme, there will be factors with specific influence to act on the precipitation qualities, the meaning and the value of them being possible to be shown only on the basis of an experimental way. Such aspects are proposed to be analysed in this paper.

3. Experimental Research

The process of $Mg(OH)_2$ preparation, starting with the magnesium chloride and dolomitic lime milk was studied within our experimental research. The reactant phase containing the magnesium chloride was reached by treating the solution at the heater from soda ash process with dolomitic lime milk. The latter was obtained by the thermical decomposition, under checked conditions, of the dolomite and the slaking of the lime.

The main characteristics of the two reactant phase are presented in Tables 1 and 2.

Table 1

Main Physical and Chemical Properties of the $MgCl_2$ Solution

	Composition / Amount	$MgCl_2$	$CaCl_2$	NH_3	NH_4Cl	NaCl
Chemical composition	g/l	12.51	44.38	0.429	1.209	88.16
	%	1.18	4.20	0.0406	0.1144	8.34
Physical properties	$\rho^0_{(l)}$, [kg/m³]			$\eta^0_{(l)}$, [N.s./m²]		
	1 057			1.2713×10^3		

Table 2

Main Physical and Chemical Properties of the Dolomitic Lime Milk

	Composition / Amount	CaO_T	MgO_T
Chemical composition	g/l	15.41	10.28
	%	1.51	1.007
Physical properties	$\rho^0_{[]susp.}$, [kg/m³]		$\eta^0_{[]susp.}$, [N.s./m²]
	1 021,1		0.9296×10^3

The double exchange process between $Ca(OH)_2$ and $MgCl_2$ was realized at a constant temperature, within an installation provided with a discontinouus reactor, by mixing. The equipment for determining the settling curves was attached to it. The experimental equipment is presented in Fig. 3.

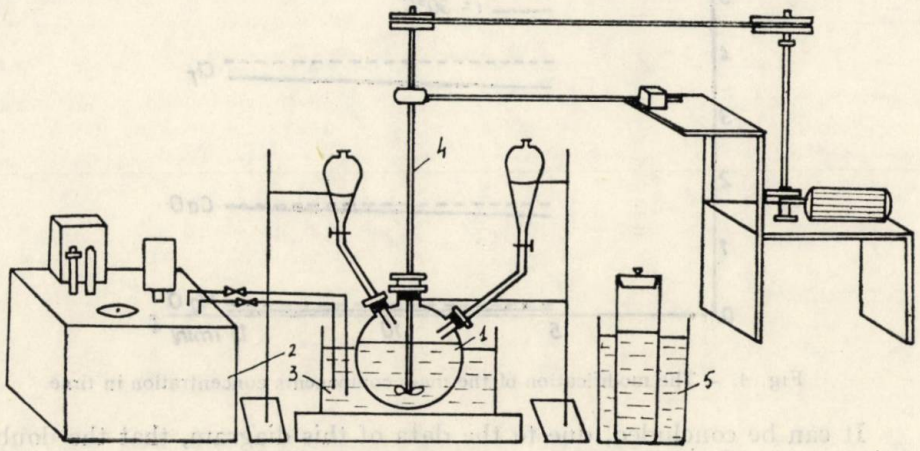


Fig. 3. — Experimental equipment.

As it can be noticed, the experimental equipment is realized of the following elements: the reactor (*1*), the thermostat (*2, 3*), the electrical stirrer (*4*), and the settling cylinders (*5*).

The double exchange process took place within two hours. The evaluation of the changes from reaction mass was made by taking out of the reactor, at certain periods of time, homogenous suspension samples, which were afterwards filtered through filters having the porosity 4. At the end of the process, suspension homogenous samples were taken out of the reaction mass into the settling cylinders. To determine the precipitate settling characteristics, the 250 ml cylinders were used, the process of settling being achieved at the same temperature at which the double exchange process took place.

The main parameters, whose influence on the process of $Mg(OH)_2$ preparation was under observation, were : work temperature, the ratio and the reactants addition rate, the influence of the presence of „initiator" crystalls in the system. The following series of experiences were executed : magnesium chloride solution added to dolomitic lime milk ($S-A$), dolomitic lime milk added to magnesium chloride solution ($A-S$), both of them mixed simultaneously at equal rate, in the presence or the absence of „initiator" crystals (S). The experiences were done at two different temperatures, i.e. 30° and 70°C, at a constant agitation with a medium speed 200 r.p.m.

4. Results and Discussion

The data concerning the process evolution, figured by means of the variation mass components concentration, were presented on the diagram : composition [%] — time (τ, min.). On the diagram from Fig. 4 the results obtained within the two studied temperatures are presented.

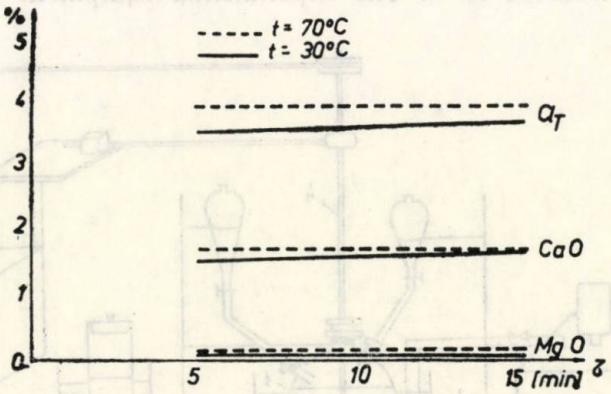


Fig. 4. — The modification of the mass components concentration in time.

It can be concluded, due to the data of this diagram, that the double-exchange reaction takes place at a sufficiently high rate so that in 5...10 min. after the process starts it can be considered as already fulfilled. This conclusion seems to be evident on the basis of the invariability, in time, of the MgO concentration within the filtrate, as well as, of the other components taken into consideration (CaO, Cl_T).

The analysis of the components concentration enabled us make the following remarks : the rapid lowering of the valuable component concentration indicates that the process develops at a high rate and most probably using the two steps mechanism (Fig. 2). Within the reaction mass, under the already mentioned work conditions, oversaturation is low, so the conditions exist for the new formed precipitate to get a microgranular structure. The increase of temperature inside the interval 30°...70°C doesn't produce sensible changes of the overall process rate and no important differences concerning the settling characteristics of the $Mg(OH)_2$ particles were evident.

The paper goes on with the results concerning the specific influence of various kinetic parameters exerced on the $Mg(OH)_2$ quality, the purity of the solid product, the particles geometry and size being included here, the appreciation relying on their sedimentation characteristics. The results are presented in Figs. 5...10 and in the Table 3. Thus, Fig. 5 shows the influence of the initial solution concentration in $MgCl_2$ exerced on the sedimentation characteristics. Figs. 6 and 7 present the influence of the way in which the reactants are mixed as well as the influence of their rate of addition on the $Mg(OH)_2$ quality. Fig. 8 shows the influence of particles increasing time on the sedimentation characteristics and Figs. 9 and 10 relate about the influence of „initiator" crystals inside the reaction mass.

Table 3

The Influence of the Kinetic Parameters on the $Mg(OH)_2$ Quality

Achievement conditions	Degrees of transformation			Solid characteristics		
	η_{NH_4Cl}	η_{MgCl_2}	$\eta_{Ca(OH)_2}$	$100\bar{x}_{Mg(OH)_2}$	$100\bar{x}_{Ca(OH)_2}$	$100\bar{x}_{CaCl_2}$
Stoichiometric amounts of reactants (simultaneously mixed)	94.5	99.6	96.7	93.8	2.41	3.70
8% $MgCl_2$ excess	93.98	91.24	97.11	93.54	2.28	3.56
20% $MgCl_2$ excess	88.20	81.30	99.50	94.70	0.05	4.86

The experimental data concerning the sedimentation characteristics were graphically represented using the following coordinates: the slurry height (H, [mm]) — time (τ, [min.]).

The overall analysis of the experimental results let us underline the following important conclusions concerning the problem under observation:

1. The $Mg(OH)_2$ suspensions obtained out of the concentrated solutions of $MgCl_2$ ($C^0_{Mg(OH)_2} \geq 10$ g/l) shows a pronounced gelatinous aspect and has a slow settling rate (Fig. 5).

2. The $Mg(OH)_2$ suspensions prepared from dilute solutions of $MgCl_2$ ($C^0_{Mg(OH)_2} \leq 10$ g/l) settles more rapidly and presents relatively clear separation surface. This result is going to complete the list of information necessary to be taken into account for the optimization analysis of the $MgCl_2$ concentration, for the process achievement on an industrial scale.

The way of reactants mixing stands for one of the most influentials factors on the $Mg(OH)_2$ quality. The precipitate settling characteristics are more improved if the precipitation takes place by means of pouring the dolomitic lime milk on the magnesium chloride solution. Higher results concerning the precipitate structure and hence, the settling rate, were obtained too as the data in Fig. 6 show, in the sequence: simultaneous adding of the reactants on the „initiator" crystals introduced in the reaction mass.

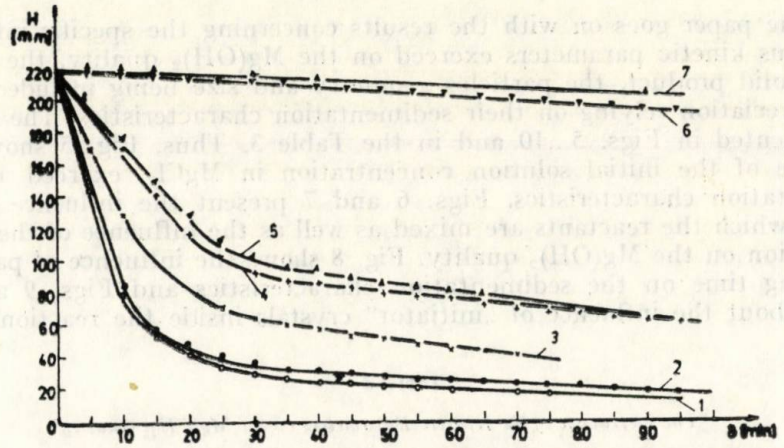


Fig. 5. — The influence of $Mg(Cl)_2$ concentration about settling characteristics of $Mg(OH)_2$ suspensions; $Mg(OH)_2$ concentration: *1* — 4.14 g/l; *2* — 4.96 g/l; *3* 6.62 g/l; *4* — 8.24 g/l; *5* — 9.10 g/l; *6* — 12.42 g/l; *7* — 16.56 g/l.

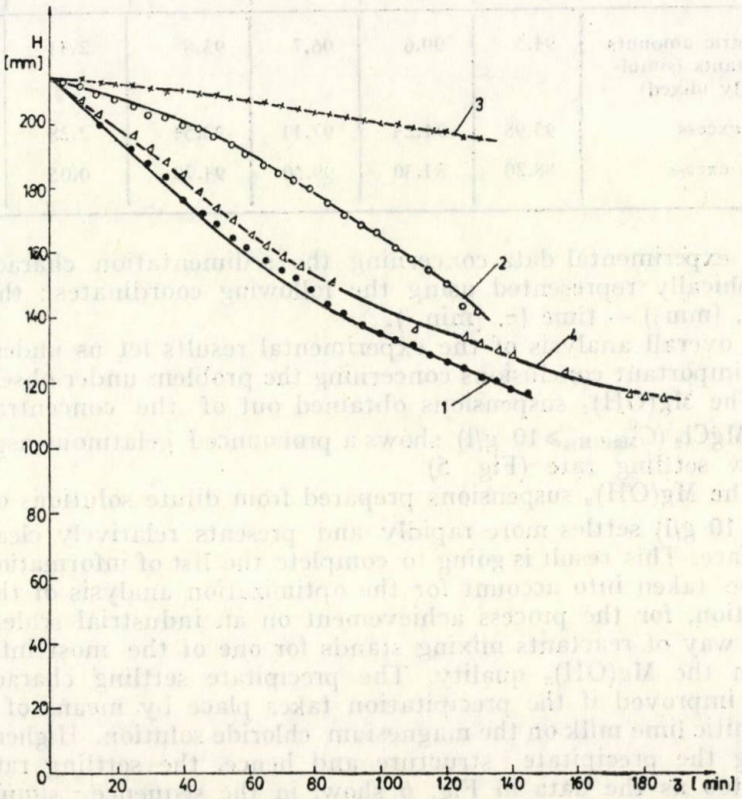


Fig. 6. — The influence of the way of introducing of the reactants; suspension types: *1* — *A* — *S*; *2* — *S* — *A*; *3* — simultaneously; *4* — simultaneously with „initiator" crystals.

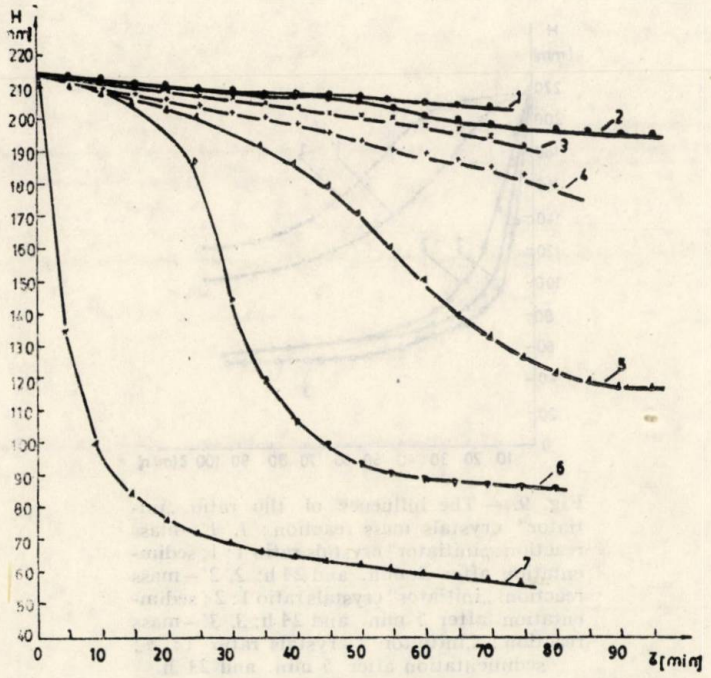


Fig. 7. — The influence of the reactants ratio: *1* — stoichiometric amounts; *2* — 8% $MgCl_2$ excess; *3* — 11% $MgCl_2$ excess; *4* — 14% $MgCl_2$ excess; *5* — 18% $MgCl_2$ excess; *6* — 20% $MgCl_2$ excess; *7* — 25% $MgCl_2$ excess.

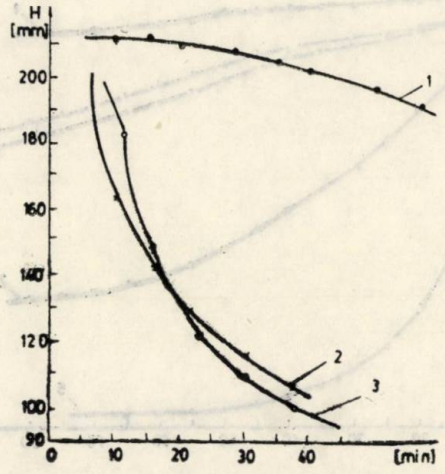


Fig. 8. — The modification of settling characteristics of $Mg(OH)_2$ suspensions with the time; settling curves after: *1* — 5 min.; *2* — 19 h; *3* — 38 h.

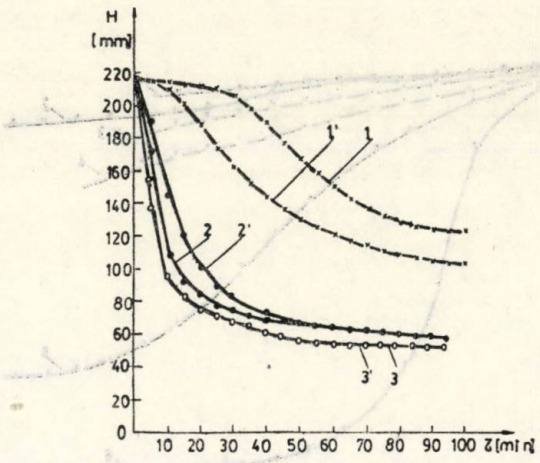


Fig. 9. — The influence of the ratio „initiator" crystals mass reaction: *1, 1'*—mass reaction: „initiator" crystals ratio 1: 1; sedimentation after 5 min. and 24 h; *2, 2'*—mass reaction: „initiator" crystals ratio 1: 2; sedimentation after 5 min. and 24 h; *3, 3'*—mass reaction: „initiator" crystals ratio 1: 4; sedimentation after 5 min. and 24 h.

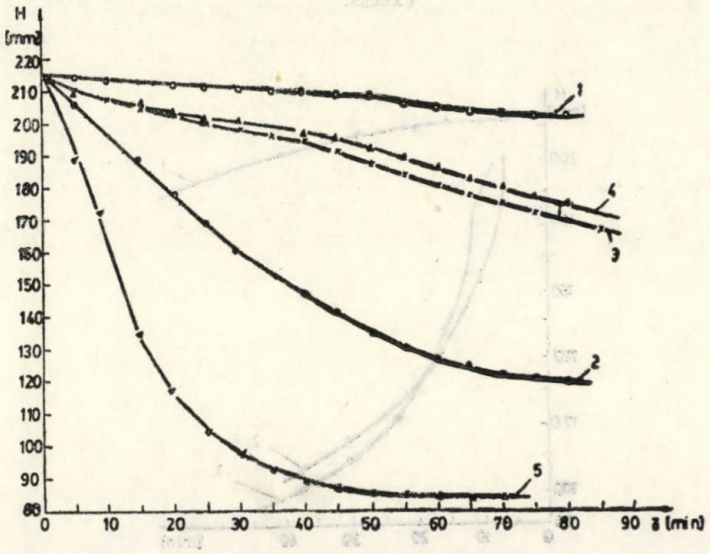


Fig. 10. — The influence of the recirculation number of „initiator" crystals: *1* — without „initiator" crystals; *2* — the first recirculation of mass reaction; *3* — the second recirculation; *4* — the third recirculation; *5* — the fourth recirculation.

The obtained experimental results regarding the used of „initiator" crystals quantity as well as the number of its recirculations (Figs. 9 and 10) show an optimum ratio „initiator" crystals : reaction mass 1 : 4 and a number of 3...4 recirculations in order to get fitted dimensions of the $Mg(OH)_2$ particles used as crystallization centers.

These results, being in agreement with data obtained by other researches [2], [8], underline the ways through which we must act in order to get an improvement in the $Mg(OH)_2$ precipitate structure. Conclusions of a special importance can be drawn too, by the analysis of those results concerning the influence of the reactants ratio on the $Mg(OH)_2$ quality. Thus, taking into account the data from Fig. 7, the utilisation of a $MgCl_2$ excess in the $Mg(OH)_2$ preparation develops as a favourable factor on the settling characteristics of $Mg(OH)_2$ and, as a consequence, on this structure.

Moreover, as the data of Table 3 show under the circumstances of an excess utilisation of $MgCl_2$ within the reaction mass, the conditions are assured for the $Mg(OH)_2$ precipitation process to take place, after the typical mechanism of : dissolving of $Ca(OH)_2$ — chemical reaction — $Mg(OH)_2$ crystals formation and growth and, as a consequence, the final product don't contain unreacted $Ca(OH)_2$ as an impurity.

The variation limits of $MgCl_2$ excess, whithin which this has a favourable behaviour, are between 20 and 25%, compared with the stoichiometric value. It is interesting to mention the fact that similar results were obtained in case of $Mg(OH)_2$ preparation, starting from sea water, as the recent data published in the literature indicate [6].

The last aspect analysed is that one, which refers to the influence of time growth of particles exerced on the sedimentation characteristics.

Studies performed in this field, though still contradictory, concerning the phenomenon explanation, are unanimous in concluding that, in time, precipitate quality is going to get improved. The optimum value of this parameter must be decided within each possibility of the process achievement.

The already mentioned conditions of the reaction mass structure, led (on the bases of the experiments), to the conclusion that the $Mg(OH)_2$ precipitate reaches the highest sedimentation values after about 40 hours. In order to establish the optimum time it is necessary to take into account the aspect which consider the possibility of adsorbtion of Ca^{2+} in stable forms on the $Mg(OH)_2$ particles and consequently the quality of the final product is modified.

5. Conclusions

The paper is dealing with a research concerning the $Mg(OH)_2$ preparation process from magnesium chloride and calcium hydroxide, inside a schema integrated with soda ash industry.

The influence of some kinetic parameters (the magnesium chloride content, the reactants ratio, the way in which these are introduced, the presence of „initiator" crystals in the reaction mass a.s.o.) on the settling characteristics of the suspensions and $Mg(OH)_2$ quality, are pointed out.

Notations

ρ	— density,	[ ]	— symbol of phase,
η	— viscosity,	*l*, susp.	— liquid, suspension,
x_{Ai}	— mass fraction,	0	— initial.
C_{Ai}	— mass concentration, [g/l],		
τ	time;		

Received, October 28, 1981

Polytechnic Institute, Jassy,
Department of Inorganic
Chemical Technology

REFERENCES

1. Ifrim L., Leonte C., Szép Al., Calistru C., Bul. Inst. polit., Iași, **XXVIII (XXXII)**, *1—4*, s. II (1983).
2. Позин М. Е., *Технология минеральных солей*. Госхимиздат, М., 1962.
3. Wolf F., Eckert L., Chemische Technik, **3**, 169 (1971).
4. Bienkiewicz G., Zesz. nauk. P.S.I., *514*, 55 (1977); Реф. Ж, **18 (II)**, **18** Л, 9 (1978).
5. Ковачев Т., Киров Г. И., Трендаферов Д., Грынчарова Е., Изв. по химия, **XII**, *2*, 267 (1979).
6. Petric B., Petric N., Chemie Ingenieur Technik, *7*, 745 (1979); Ibid., *10*, 985 (1979).
7. Kanungo S. B., De P. K., Basu U. P., Indian J. of Technol., *1*, 123 (1970); Ibid., *2*, 71 (1970); Ibid., *5*, 180 (1970).
8. Winnacker K., Kühler L., *Tehnologie chimică anorganică*, (transl. from German). Ed. Tehn., Buc., 1962.
9. Calistru C., Leonte C., *Tehnologia substanțelor anorganice*. E.D.P., Buc., 1972.

CERCETĂRI DE INGINERIE CHIMICĂ ÎN CADRUL PROCESULUI DE OBȚINERE A $Mg(OH)_2$

II. Studii privind influența unor parametri cinetici asupra caracteristicilor produsului solid

Se continuă seria cercetărilor consacrate procesului obținerii $Mg(OH)_2$ plecînd de la $MgCl_2$ și $Ca(OH)_2$ în cadrul unei scheme tehnologice grefate pe industria sodei amoniacale. În cadrul cercetării se pun în evidență influențele principalilor parametri cinetici (conținutul de clorură de magneziu, raportul reactanților, modul de contactare a acestora, prezența amorsei în masa de reacție ș.a.) asupra caracteristicilor de sedimentare și a calității $Mg(OH)_2$.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secția II
CHIMIE și INGINERIE CHIMICĂ

C.Z. 661.521

CERCETAREA PROCESULUI DE SUBLIMARE A CLORURII DE AMONIU

I. MODELAREA PROCESULUI

DE

Al. SZÉP, C. CALISTRU și LIVIA IFRIM

1. Introducere

Dezvoltarea extensivă a industriei sodei calcinate din țara noastră este în mare măsură condiționată de poluarea mediului cu soluții reziduale provenite din actualul procedeu Solvay, precum și de faptul că tehnologia respectivă permite valorificarea doar a 75% din sodiul existent în materia primă, întreaga cantitate de clor și 25% de sodiul din materia primă fiind pierdute prin deversarea, sub formă de soluții, în emisari [1]...[3]. Avînd în vedere aceste incoveniente majore precum și faptul că țara noastră dispune de cantități importante de sare gemă, ce trebuie valorificate în mod rațional, s-au întreprins o serie de cercetări de inginerie chimică pentru elaborarea unui procedeu modificat care să permită valorificarea complexă și completă a acestei bogății naturale. În cadrul procedeelor respective [4]...[9] o parte își propun valorificarea componenților sării geme sub forma sodei calcinate și a clorurii de amoniu solide ca produs intermediar. Avînd în vedere că în prezent clorura de amoniu are o utilizare restrînsă (industria metalurgică, industria electrotehnică, industria chimică) aplicarea unuia din procedeele propuse este condiționată de lipsa unui beneficiar ce ar putea utiliza cantitățile mari din acest produs. De aceea, în paralel cu cercetările pentru elaborarea unui nou procedeu de valorificare a sării geme s-au întreprins și cercetări teoretice și experimentale pentru transformarea clorurii de amoniu solide în clorură de calciu și/sau magneziu, produse cu o mai mare posibilitate de utilizare în economia națională.

Deoarece în procesul transformării clorurii de amoniu solide în clorură de calciu (sau magneziu) un rol important îl are procesul de sublimare a clorurii de amoniu [10]...[13], în această lucrare se prezintă cercetările teoretice și experimentale privind mecanismul și modelarea acestui proces.

2. Mecanismul macrocinetic al procesului de sublimare a clorurii de amoniu

Procesul sublimării clorurii de amoniu este considerat, în cercetările menționate în literatura de specialitate [10]...[15], ca un proces relativ complex. Astfel, la nivelul mecanismului procesului de sublimare, punctele de vedere exprimate sînt contradictorii : după unii autori procesul se desfășoară ca un proces tipic de sublimare, după alții se consideră că sublimarea este urmată sau însoțită de disocierea termică a clorurii de amoniu solide sau gazoase [10]...[14]. Acest din urmă punct de vedere se bazează pe măsurătorile efectuate privind proprietățile fazei gazoase (densitate, vîscozitate) precum și pe reactivitatea avansată a acesteia. Luînd în considerare

aceste aspecte se pot stabili următoarele două variante posibile privind mecanismul macrocinetic de desfășurare a procesului de sublimare :

I. Procesul se desfășoară cu formarea acidului clorhidric, a amoniacului și a clorurii de amoniu gazoase.

Ecuația caracteristică care redă structura fazelor reactant și produs de reacție are forma :

$$(1) \qquad [NH_4Cl]_s \rightarrow [NH_4Cl]_s + [NH_4Cl + NH_3 + HCl]_g.$$

Procesele elementare independente pe care aceasta le include sînt :

$$(2) \qquad [NH_4Cl]_s \rightleftarrows [NH_4Cl]_g, \qquad (3) \quad [NH_4Cl]_g \rightleftarrows [NH_3]_g + [HCl]_g.$$

II. Procesul de sublimare se desfășoară cu formarea acidului clorhidric și a amoniacului în faza gazoasă. Ecuația caracteristică corespunzătoare are forma :

$$(4) \qquad [NH_4Cl]_s \rightarrow [NH_4Cl]_s + [HCl + NH_3]_g.$$

Procesul elementar independent pe care aceasta îl include este de forma :

$$(5) \qquad [NH_4Cl]_s \rightleftarrows [NH_3]_g + [HCl]_g.$$

Stabilirea variantei care exprimă mecanismul real al procesului constituie o operație destul de dificilă din cauza lipsei datelor cu privire la proprietățile componenților fazelor gazoase și din cauza lipsei metodelor adecvate de analiză a fazei gazoase.

Se poate adopta drept punct de plecare, pentru stabilirea variantei celei mai probabile după care se desfășoară procesul studiat, următoarea : dacă procesul real se desfășoară după una din cele două variante (I sau II), atunci datele experimentale cu privire la presiunea totală a fazei gazoase la echilibru vor trebui să coincidă, în limita erorilor acceptate, cu presiunea totală la echilibru calculată pe baza datelor termodinamice pentru cele două variante. Compararea celor două seturi de valori, obținute pe căi diferite, va servi drept criteriu de alegere a variantei celei mai probabile.

În acest scop, în prima etapă s-au preluat din literatură [11], [12], [14] datele experimentale ale lui Smith-Henzies, Colvert și Lamberd referitoare la variația cu temperatura a presiunii totale la echilibru. Aceste date sînt prezentate în tabelul 1.

În continuare, cu ajutorul acestora s-au calculat valorile presiunii totale deasupra sistemului. Pentru calculul presiunii totale de echilibru s-au considerat cele două variante și s-au explicitat relațiile de calcul, utilizînd metoda constantei de echilibru.

Astfel în cazul variantei I s-au definit constantele de echilibru ale celor două procese elementare (2), (3) notate cu K_{p2}, K_{p3} :

$$(6) \qquad K_{p2} = \frac{P_{NH_4Cl}}{a_{NH_4Cl}}, \qquad (7) \qquad K_{p3} = \frac{P_{HCl} P_{NH_3}}{P_{NH_4Cl}}.$$

Cunoscînd că :

$$(8) \qquad a_{NH_4Cl} = 1, \quad P_{HCl} = P_{NH_3}$$

Tabelul 1

Variația presiunii totale la echilibru deasupra clorurii de amoniu funcție de temperatură

T °K	p_{tot}, [atm.]		
	Smith-Henzies	Smith-Colvert	Smith-Lamberd
523	–	0,06513	–
553	0,1815	0,17760	–
563	0,18289	–	0,2438
573	0,3315	–	0,3322
583	0,4420	0,4490	0,4490
593	0,5880	–	0,6386
603	0,7723	0,8034	0,8000
606,5	0,8447	–	–
610	–	1,00	–
618	–	1,2197	–
623	–	1,3987	–

rezultă pentru presiunea parțială expresia :

$$P^e_{NH_3} = P^e_{HCl} = \sqrt{K_{p2}K_{p3}} \tag{9}$$

și pentru presiunea totală

$$P^e_T = P^e_{HCl} + P^e_{NH_3} + P^e_{NH_4Cl} = 2\sqrt{K_{p2}K_{p3}} + K_{p2}. \tag{10}$$

În cazul variantei II, definind constanta de echilibru :

$$K_{p5} = \frac{P_{HCL}P_{NH_3}}{a_{NH_4Cl}} \tag{11}$$

și ținînd seama de (8) se obține relația de calcul a presiunii totale la echilibru :

$$P^e_T = P^e_{HCl} + P^e_{NH_3} = 2\sqrt{K_{p5}}. \tag{12}$$

Pentru determinarea valorilor numerice ale constantelor de echilibru s-a utilizat metoda de calcul bazată pe variația entalpiei libere de proces ($\Delta_R G^0_T$) [1]. Datele necesare calculelor, preluate din literatură [10]...[15], sînt prezentate în tabelul 2.

Pe baza datelor termodinamice din tabelul 2 s-au calculat, în primul rînd, efectele termice ale proceselor, entalpiile libere de reacție iar apoi s-au determinat expresiile de calcul ale constantelor de echilibru. Datele obținute sînt prezentate în tabelul 3.

Tabelul 2

Date termodinamice ce caracterizează componenții sistemului

Componentul	Faza	Starea	H_f^0 cal/mol.	S_m^0 cal/mol. grad	C_p cal/mol. grad
NH_4Cl	s	α	$-74\,950$	31,8	$9,8 + 0,03685\,T$
		β	—	—	$5,0 + 0,034\,T$
	g	—	$-42\,400$	—	—
NH_3	g	—	$-11\,000$	45,91	$5,2+0,008963T+1,764.10^{-6}T^2$
HCl	g	—	$-22\,063$	44,66	$6,7+0,00084\,T$

Tabelul 3

Expresiile de calcul ale efectelor termice, entalpiilor libere și ale constantelor de echilibru pentru procesele elementare

	Procesul	Forma expresiei	Obs.
$\Delta_{R_i} H_{288}^0$	(2)	32 550	
	(3)	9 337	
	(5)	41 887	
$\Delta_{R_i} G_T^0$	(2)	—	lipsesc datele experimentale
	(3)	—	
	a'	$41\,887 - 58,57\,T$	$T=298°K$
	(5) b'	$42\,263 - 55,95\,T - 0,0135235\,T^2 - 0,1588 . 10^{-6} T^3$	$T<457°K$
	c'	$40\,706,2 - 51,15\,T - 0,0120985\,T^2 - 0,588 . 10^{-6} T^3$	$T>457°K$
$\lg K_{p_i}$	(2)	—	
	(3)	—	
	a	$12,842923 - 9\,153,51\,T^{-1}$	$T=298°K$
	(5) b	$12,299+2,95606 . 10^{-3}\,T + 1,2853 . 10^{-7} T^2 - 9\,238,161\,T^{-1}$	$T<457°K$
	c	$11,1807 + 2,64457 . 10^{-3}\,T + 1,2853 . 10^{-7} T^2 - 9\,897,841\,T^{-1}$	$T>457°K$

După cum se poate constata din datele prezentate în tabelele 2 și 3, mărimile termodinamice existente în literatură permit calculul valorii constantei de echilibru doar pentru procesul (5), deci pentru varianta II referitoare la mecanismul sublimării. În intervalul de temperatură cuprins în tabelul 1, utilizînd relațiile (5 *a*) și (5 *b*), s-au calculat valorile presiunii totale la echilibru, valori care s-au reprezentat grafic în paralel cu valorile experimentale preluate din literatură (fig. 1).

Din datele reprezentate în fig. 1 se constată că diferitele valori experimentale preluate din literatură se suprapun pe un domeniu larg de temperatură (553°...613°K), ceea ce atestă precizia acestora. Datele cal-

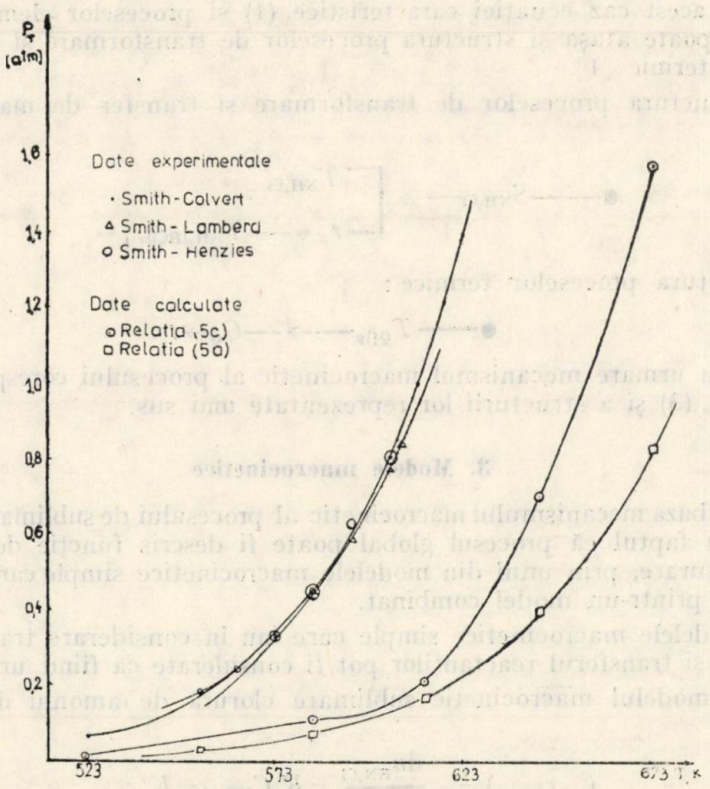


Fig. 1

culate pe baza relațiilor (5 *a*) și (5 *c*) diferă destul de mult între ele, mai ales la temperaturi depășind 613°K, ceea ce subliniază faptul că renunțarea la variația cu temperatura a efectului termic și a entropiei de reacție (cazul (5 *a*)) duce la erori apreciabile. Compararea datelor exprimate cu cele calculate pentru varianta II arată că diferențele mari care apar nu pot fi puse pe seama erorilor experimentale, ci se datoresc diferenței de mecanism macrocinetic.

Pentru o anumită valoare a temperaturii se poate scrie inegalitatea $(P^e_T)_E > (P^e_T)_C$ și respectiv

$$(P^e_T)_E = (P^e_T)_C + \Delta p. \tag{13}$$

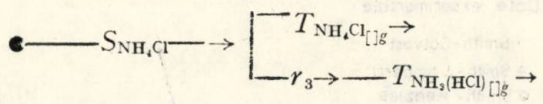
Făcînd apel la varianta I, relația (13) poate fi scrisă sub forma

$$(P^e_{NH_3})_E + (P^e_{HCl})_E + (P^e_{NH_4Cl})_E = (P^e_{NH_3})_C + (P^e_{HCl})_C + \Delta p. \tag{14}$$

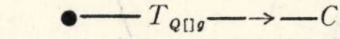
De aici se poate constata că diferența Δp nu reprezintă altceva decît presiunea parțială la echilibru a NH_4Cl, deci procesul real nu se desfășoară pe baza variantei II ci pe baza variantei I.

În acest caz ecuației caracteristice (1) și proceselor elementare (2), (3) li se poate atașa și structura proceselor de transformare și transfer de masă și termic [1].

Structura proceselor de transformare și transfer de masă este de forma :



iar structura proceselor termice :



Prin urmare mecanismul macrocinetic al procesului corespunde relațiilor (1)...(3) și a structurii lor reprezentate mai sus.

3. Modele macrocinetice

Pe baza mecanismului macrocinetic al procesului de sublimare se poate evidenția faptul că procesul global poate fi descris funcție de condițiile de desfășurare, prin unul din modelele macrocinetice simple care se constituie sau printr-un model combinat.

Modelele macrocinetice simple care iau în considerare transformarea de masă și transferul reactanților pot fi considerate ca fiind următoarele :

a) modelul macrocinetic sublimare clorură de amoniu definit prin ecuația :

$$(-\bar{r}_{NH_4Cl}) = -\frac{dn_{HN_4Cl}}{s\,d\tau} = K_s C_{NH_4Cl} = K' ; \tag{15}$$

b) modelul macrocinetic transfer clorură de amoniu prin faza gazoasă, avînd expresia :

$$(-\bar{q}_{NH_4Cl}) = K_{T_{NH_4Cl}}(p^{(cs)}_{NH_4Cl} - p^{(g)}_{NH_4Cl}) ; \tag{16}$$

c) modelul macrocinetic reacție de descompunere termică a clorurii de amoniu în fază gazoasă :

$$(-r_{NH_4Cl}) = K_1 C^{o}_{HCl} C^{m}_{NH_4Cl} - K_2 C^{n'}_{HCl} C^{m'}_{NH_3} ; \tag{17}$$

d) modelul macrocinetic de transfer acid clorhidric (respectiv amoniac) prin faza gazoasă, definit prin relația :

$$(-\bar{q}_{HCl(NH_3)}) = K_{T_{HCl(NH_3)}}(p^{(cr)}_{HCl(NH_3)} - p^{(g)}_{HCl(NH_3)}). \tag{18}$$

Modelele macrocinetice simple care iau în considerare transferul și consumul de căldură pot fi considerate următoarele :

e) modelul macrocinetic transfer de căldură prin faza gazoasă :

$$(-\bar{q}_Q) = K_{T_Q}(T^{(g)} - T^{(s)}) ; \tag{19}$$

f) modelul macrocinetic consum de căldură, definit prin relația :

$$(-\bar{r}_Q)=(\overline{\Delta_R H})(-\bar{r}_{NH_4Cl}). \tag{20}$$

În afară de modelele macrocinetice simple, în desfășurarea procesului global un rol însemnat îl pot avea și modelele macrocinetice combinate de forma : sublimare clorură de amoniu — transfer clorură de amoniu prin faza gazoasă, sublimare clorură de amoniu — disociere termică — transfer produși de reacție, transfer căldură — sublimare clorură de amoniu ș.a. Ecuațiile modelelor macrocinetice combinate se stabilesc plecînd de la modelele macrocinetice simple, după o metodică cunoscută [1], de egalare a vitezelor acestora. Astfel pentru modelul macrocinetic combinat sublimare clorură de amoniu — transfer clorură de amoniu prin faza gazoasă, ecuația modelului macrocinetic are forma :

$$-\bar{r}=\frac{1}{1/K_s+1/K_{T_{NH_4Cl}}}\,p^{(g)}_{NHCl_4}\,. \tag{21}$$

4. Modelarea matematică

Pentru elaborarea modelelor matematice capabile să permită descrierea cantitativă a procesului la desfășurarea acestuia în raport cu fiecare din modelele macrocinetice luate în considerare, se va alege drept element

Tabelul 4

Modelele matematice ale procesului de sublimare

Tipul modelului macrocinetic	Modelul matematic	
	Forma diferențială	Forma integrală
S_{NH_4Cl}	$\frac{\rho^* R}{3(1-\eta)^{2/3}}\cdot\frac{d\eta}{d\tau}=Kp_{NH_4Cl_{[]_g}}$	$\tau=\frac{\rho^* R}{Kp_{NH_4Cl}}\,[1-(1-\eta)^{1/3}]$
$T_{NH_4Cl_{[]_g}}$	$\frac{\rho^* R}{3(1-\eta)^{2/3}}\cdot\frac{d\eta}{d\tau}=K_{T_{NH_4Cl}}\Delta p_{NH_4Cl}$	$\tau=\frac{\rho^* R}{K_{T_{NH_4Cl}}\Delta p_{NH_4Cl}}\,[1-(1-\eta)^{1/3}]$
r_{NH_4Cl}	$-\frac{dn_{NH_4Cl}}{V d\tau}=K_1 p^{0}_{HCl}\,p^{m}_{NH_4Cl}-K_2 p^{n'}_{HCl}\,p^{m'}_{NH_3}$	—
T_Q	$\rho^* R\,\frac{d\eta}{3(1-\eta)^{2/3}d\tau}=K_{T_Q}\Delta T$	$\tau=\frac{\rho^* R}{K_{T_a}(T_{[]_g}-T)}\,[1-(1-\eta)^{1/3}]$
$S-T_{NH_4Cl}$	$\frac{\rho^* R}{3}\cdot\frac{d\eta}{(1-\eta)^{2/3}d\tau}=K_G p_{NH_4Cl_{[]_g}}$	$\tau=\frac{\rho^* R}{K_G p_{NH_4Cl_{[]_g}}}\,[1-(1-\eta)^{1/3}]$

de structură a masei de reacție granula de solid. Ecuațiile de bilanț care exprimă transformarea reactantului din elementul macrostructural solid sînt

$$-\frac{dn_{NH_4Cl}}{s\,d\tau} = -\rho^* \frac{dr}{d\tau}, \tag{22}$$

în condițiile aprecierii transformării prin variația razei granulei sau:

$$-\frac{dn_{NH_4Cl}}{s\,d\tau} = \frac{\rho^* R\, d\eta_{NH_4Cl}}{3(1-\eta_{NH_4Cl})^{2/3} d\tau}, \tag{23}$$

în condițiile aprecierii transformării prin η_{NH_4Cl}.

Ținînd cont de relațiile (22), (23) și de modelele macrocinetice stabilite anterior, s-au elaborat modelele matematice ale procesului de sublimare. Acestea sînt reprezentate în tabelul 4.

5. Concluzii

1. Se prezintă rezultatele cercetărilor întreprinse în vederea stabilirii mecanismului macrocinetic real după care se desfășoară procesul de sublimare a clorurii de amoniu. Pe baza analizei efectuate s-a stabilit că procesul de sublimare are loc după mecanismul sublimare clorură de amoniu — descompunerea parțială a clorurii de amoniu în faza gazoasă — transfer produși de reacție.

2. Se realizează modelarea macrocinetică și matematică a procesului stabilindu-se modelele macrocinetice simple și combinate prin intermediul cărora se va putea trece la descrierea cantitativă a procesului în diferitele condiții de realizare a acestuia. Modelele matematice stabilite au la bază modelul matematic al elementului macrostructural — granula de solid.

Notații

K_{p_i} — constanta de echilibru a proceselor elementare, ($i = 2, 3, 5$), exprimată în presiuni parțiale;

p_{A_i} — presiunea parțială a componentului A_i (NH_3, NH_4Cl, HCl);

a_{NH_4Cl} — activitatea clorurii de amoniu solide;

$\Delta_{R_i} H^0_{298}$ — efectul termic al procesului elementar i determinat la temperatura 298°K;

H^0_f — entalpia de formare standard;

S^0_m — entropia molară standard;

$C_p(T)$ — căldura specifică molară la presiune constantă;

Δp — diferență de presiune;

S — suprafața de sublimare, de transfer;

n, m, n', m', — ordinele parțiale de reacție;

r — raza granulei la un moment dat;

ρ^* — densitatea molară;

R — raza inițială a granulei;

$-r_{NH_4Cl}$ — viteza procesului de sublimare;

$-q_{NH_4Cl}$; $-q_{HCl(NH_3)}$ — viteza procesului de transfer a clorurii de amoniu, respectiv a acidului clorhidric au amoniacului prin volumul fazei gazoase;

$-r_{NH_4Cl}$ — viteza procesului de descompunere a clorurii de amoniu;

$-\overline{q_Q}$ — viteza procesului de transfer de căldură;
$-r_Q$ — viteza procesului de consum de căldură;
K_S — constanta vitezei procesului de sublimare;
$K_{T_{NH_4Cl(NH_3, HCl)}}$ — constanta vitezei procesului de transfer a NH_4Cl, HCl, NH_3 prin volumul fazei gazoase;
K_1, K_2 — constanta vitezei reacţiei directe şi inverse;
K_{T_Q} — constanta vitezei procesului de transfer de căldură;
$\overline{\Delta_R H}$ — efectul termic mediu;
K_G — constanta vitezei procesului global definită de relaţia $1/K_G = 1/K_S + 1/K_{T_{NH_4Cl_{[]_g}}}$;
$T_{[]_g}$ — temperatura fazei gazoase;
T_{pr} — temperatura procesului de sublimare;
n_{A_i} — numărul de moli de component;
$p^{es}_{NH_4Cl}$ — presiunea parţială a clorurii de amoniu la echilibrul de fază;
p^{er}_{HCl} — presiunea parţială a acidului clorhidric la echilibrul reacţiei.

Indici şi simboluri

$[]_{g(s)}$ — simbolul fazei gazoase (solide);
$\bullet\!-\!\!\rightarrow$ — simbolul procesului elementar (S_{NH_4Cl} — sublimare, r_3 — reacţia (3), $T_{NH_4Cl_{[]_g}}$ — transferul NH_4Cl prin faza gazoasă);
C_Q — consum de căldură;
E — experimental;
C — calculat;
e — echilibru.

Primită la 1 decembrie 1981

Institutul politehnic, Iaşi,
Catedra de tehnologia substanţelor
anorganice şi a materialelor de construcţii

BIBLIOGRAFIE

1. Calistru C., Leonte C., *Tehnologia substanţelor anorganice*. EDP, Buc., 1972.
2. Щокин И. Н., Кращенинников С. А., *Технология соды*. Изд. Химия, М., 1975.
3. Rant Z., *Die Erzeugung von Soda, nach dem Solvay Verfahren*. Tuzla, Sarajevo, 1965.
4. Calistru C. ş.a., Brevet R.S.R., *67 243* (1978).
5. Calistru C. ş.a., Brevet R.S.R., *67 812* (1978).
6. Calistru C., LeonteC., Ifrim L., Szép Al., Rev. de chimie, **30**, *5*, 439 (1979).
7. Calistru C., Leonte C., Ifrim L., Szép Al., Bul. I-lui Congres Naţional de chimie, Buc., 1978, 224.
8. Calistru C., Leonte C., Ifrim L., Szép Al., *Procedeu de fabricare a sodei şi clorurii de amonid*. Simp. IITPIC, Buc., mai 1980.
9. Calistru C., Leonte C., Ifrim L. Szép Al., *Analiza posibilităţilor de obţinere şi valorificare a clorurii de amoniu*. Lucrare comunicată la cel de al II-lea Congres Naţional de chimie, 7—10 sept. 1981, Buc.
10. Străjescu M. ş.a., Rev. de chimie, **32**, *7*, 649 (1982).
11. Pascal P., *Nouveau traité de chimie minerale*. Vol. **V**, Paris, 1965.
12. * * * *Gmelius Handbuch der anorganischen Chemie*. Bd. **VII**, Heidelberg—Berlin, 1936
13. * * * *Manualul inginerului chimist*. Vol. **II**, Ed. Tehn., Buc., 1951.
14. * * * *Ullmanns Enziklopädie der tehnischen Chemie*. Bd. **3**, Schwarzenberg, München, 1953, 607.

15. Брицке Е. В., *Термические константы неорганических веществ*. Изд. АН СССР, М. -Л., 1949.
16. Landolt Börnstein, *Zahlenwerte und Funktion aus Physik, Chemie, Astronomie Geophysik, Technik*. Bd. 2, Springer Verlag, Berlin-Göttingen-Heidelberg, 1961.
17. Пешковский В. В., Звездин А. Д., Сб. науч. тр. Перм. политехн. инст., 18, 33—41 (1965).
18. Levenspiel O., *Tehnica reacţiilor în ingineria chimică*, (trad. din l. germană). Ed. Tehn. Buc., 1967.

STUDY OF THE AMMONIUM CHLORIDE SUBLIMATION PROCESS

I. Process Modelling

(Summary)

The results of the studies concerning the sublimation process of ammonium chloride are presented. Taking into account the data previously published in the special literature, the sublimation process mechanism was determined by the method of chemical equilibrium analysis.

On the basis of proposed mechanismus (sublimation—partial descomposition of ammonium chloride) the modelling of process was effectuated and simple and combinated macrokinetic models has been proposed ; in the same time mathematical modell are also obtained.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

D.C. 66.093.6

STUDIES ON KINETICS OF PHENOXYACETIC ACID DRYING

BY

GH. CRISTIAN, CORNELIU ONISCU, IOSIF MIHALY and I. IŞTOAN

1. Introduction

During drying a grain layer, by passing the drying agent over the material surface, the drying rate exhibites a constant period and one or two periods of decreasing rate, or only continuously decreasing rate. During the constant period the moisture evaporation takes place at the material surface bathed by the drying agent. The magnitude of evaporation rate is comparable to that at the free liquid surface. During the whole constant period the material surface is fed with moisture from inside, due to the capillarity forces. The drying process is controlled by the evaporation rate and the resistance of the surface boundary layer.

During the period of decreasing rate the evaporation surface shifts within the layer, the moisture migration rate being lower than the evaporation rate. In this case the drying process is controlled by the evaporation rate, the resistance towards the vapour diffusion through the material layer and the external boundary layer. In most cases the duration of drying process is determined by the drying rate during the decreasing rate period. To shorten the drying time one should increase the moisture migration rate towards the material surface, where the moisture evaporation takes place during the constant rate period [1].

In the present paper an experimental study concerning the drying of phenoxyacetic acid by passing the drying agent over the material surfacc is reported. The moisture migration through the layers of phenoxyacetie acid was also investigated, an equation for calculating the migration coefficient being finally derived.

2. Experimental

The experimental runs were performed on a laboratory installation [2]. The phenoxyacetic acid to be dried was placed in a parallepipedic tray $70 \times 51 \times 20$ mm, thermally isolated on five faces by a thick thermoisolating layer. The drying was accomplished by passing the drying agent over the material surface. The material layers were previously moisted till a well settled humidity. To determine the variation in time of material moisture a balance was used, the experimental material sample being hanged on one arm. Before starting the experimental runs, the drying equipment was brought to a steady state regime. The time required for evaporating a certain amount of moisture, under the experimental conditions, was determined by means of a chronometer. The obtained data were used for calculating the drying rate. To determine the moisture distribution within the material during drying, a gravimetrical method was used [3], [4].

3. Experimental Results

3.1. Drying Phenoxyacetic Acid

The phenoxyacetic acid obtained in pilot equipment was purified for removing the unreacted phenol, filtered and dried. The drying was accomplished by passing the drying agent over the material surface. The drying agent parameters influencing the process are : temperature, relative humidity and rate. These parameters acts not only on the drying rate but also on the critical moisture of material, as well as on its technological properties and quality. That's why is necessary to find such a drying regime that in a relatively short time, with a minimum heat consumption, to obtain the dried material having the required technological properties.

Of the air parameters influencing the drying process the temperature and flowing rate were investigated. In the present paper the experiments were carried out at three different temperatures, namely : 40°, 50° and 60°C, respectively with an air flowing rate of 1.72 m/s. The obtained results are plotted in Fig. 1.

As can be seen in Fig. 1 the drying rate increases with increasing temperature while the process duration diminishes. The drying rate is mostly influenced during the period of constant rate.

To investigate the influence of air rate on the drying process the experimental runs were carried out at two flowing rates : 1.72 and 2.6 m/s, respectively, at a temperature of 50°C. The obtained results are plotted in Fig. 2.

As can be seen in Fig. 2 the drying rate increase with increasing air rate. This influence is more clear during the period of constant rate drying and less significant during that of decreasing rate. The decrease of the air rate influence during the period with decreasing rate can be accounted for by the displacement of the evaporation surface within the material which determines the occurence of an additional resistance to that of the film at the surface corresponding to the period with constant rate. The air rate influences the drying rate by means of the boundary film at the surface. When the resistance of the latter in the drying process begins to lower compared to the resistance of the material layer, which becomes prevailing, the air rate is expected not to have the same influence as during the period of constant rate. During the first period of drying the resistance of the air film at the material surface is controlling the process.

3.2. Moisture Distribution within the Phenoxyacetic Acid Layers

In the drying process, due to moisture evaporation at the material surface, a moisture gradient occur over the material thickness which determine the moisture migration towards the drying surface. In this case a continuous redistribution of moisture and capillary effects becomes possible. The moisture distribution within the material during drying is a function of the coefficient of moisture migration in liquid state, known also as coefficient of diffusion.

In the drying process development the coefficient of diffusion is a determining factor in addition to the external conditions. It depends on both temperature and the moisture content. The dependence on the mois-

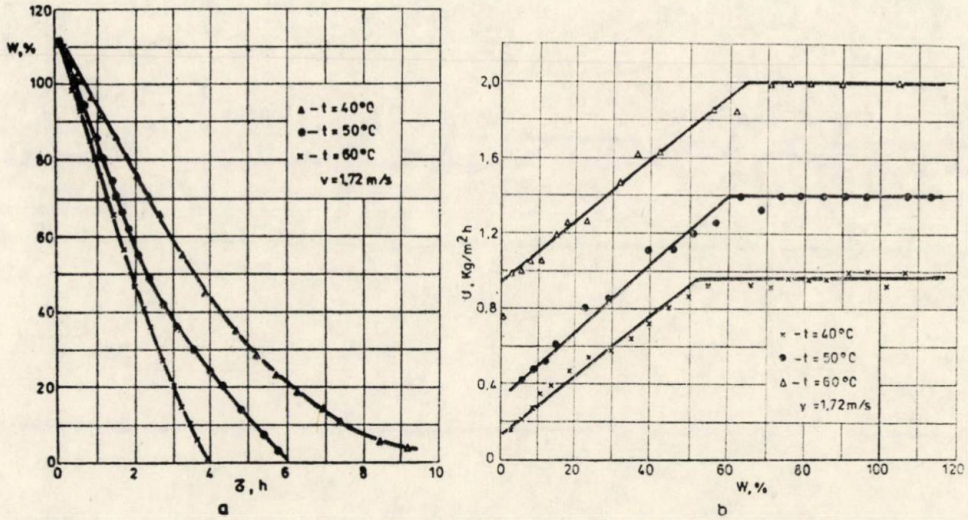


Fig. 1. — Kinetics of drying of layers of phenoxyacetic acid : *a* — variation of material moisture in time ; *b* — variation of drying rate vs. moisture.

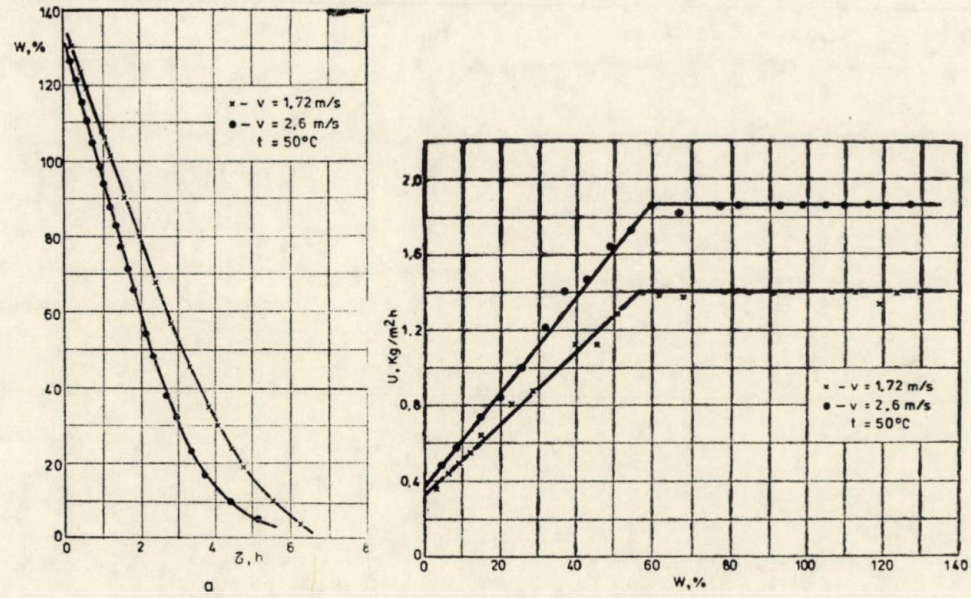
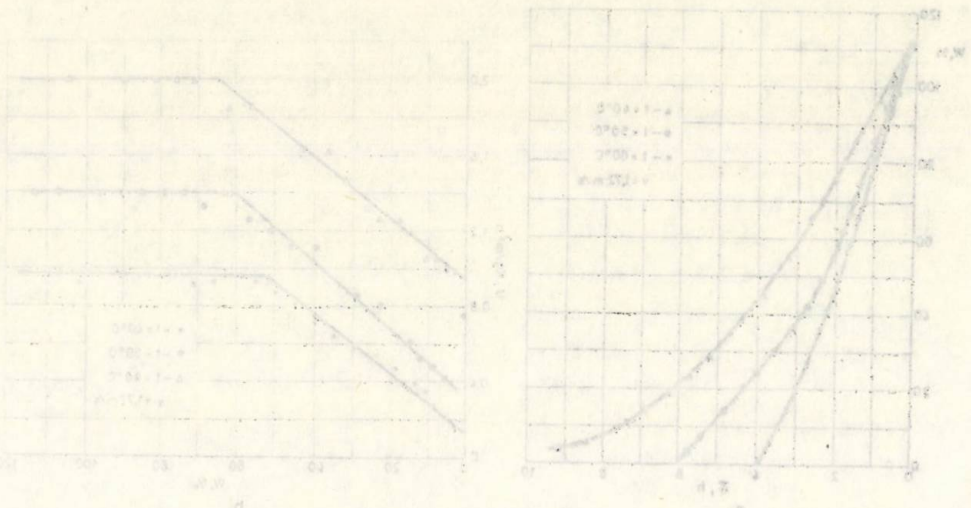
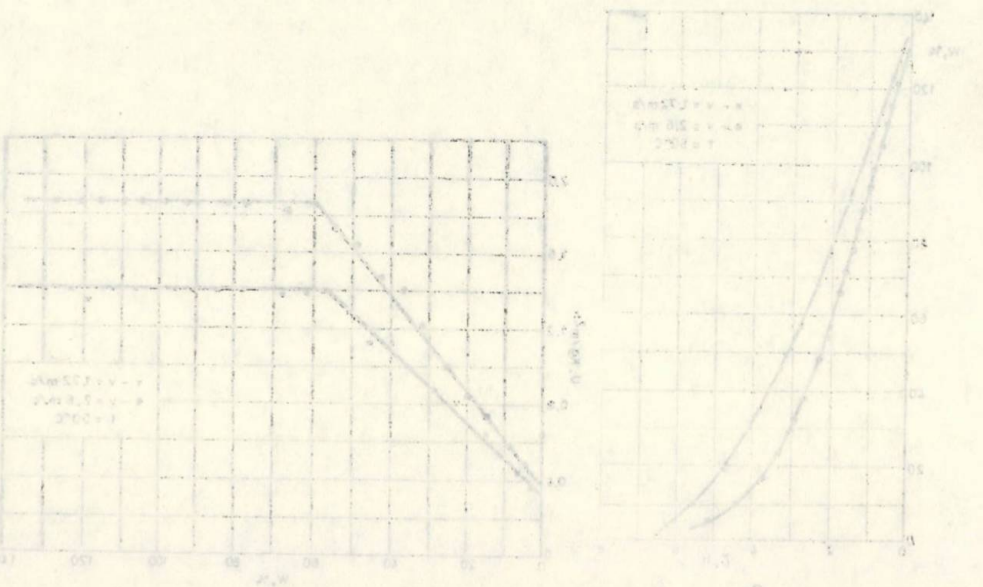


Fig. 2. — Influence of rate on the drying kinetics of the phenoxyacetic acid layers : *a* — material moisture variation in time ; *b* — drying rate vs. moisture content.





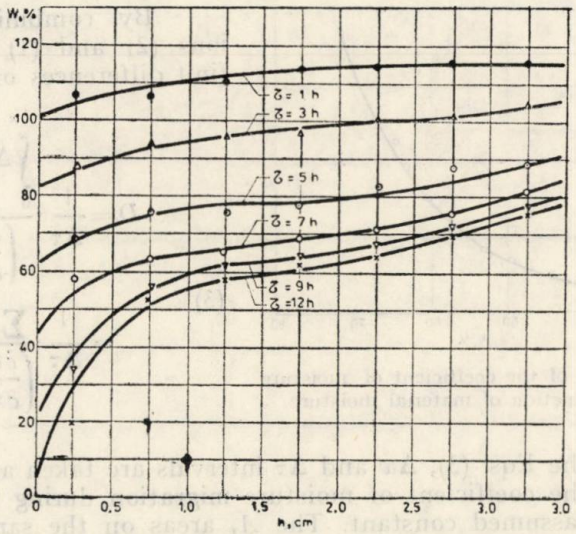


Fig. 3. — Curves of moisture distribution within the material.

ture content was determined by measuring the profile of moisture concentration within the material after a certain time.

For determining the local moisture content the gravimetrical method was used. The results obtained after 12 hours of drying are given in Fig. 3.

The migration coefficient can be determined grapho-analytically [2], [4]. In this view one starts from the equation of mass transfer in one direction, which integrated with the condition leads to the equation :

$$D = \frac{\int_0^x \frac{\partial w}{\partial \tau}\, dx}{\left(\frac{\partial w}{\partial x}\right)_x}. \tag{1}$$

The terms appearing in Eq. (1) could be calculated grapho-analytically if the curves of moisture distribution weree known. Thus $\int \frac{\partial w}{\partial \tau}\, dx$ represent the surface between the two adiacent curves and time period $d\tau$, (Fig. 4).

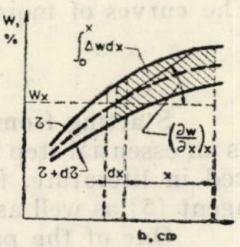


Fig. 4. — Determination of the moisture migration coefficient by a grapho-analytical procedure.

In this case it can be written :

$$\int_0^x \frac{\partial w}{\partial \tau}\, dx = \frac{1}{\Delta \tau} \int_0^x \Delta w\, dx. \tag{2}$$

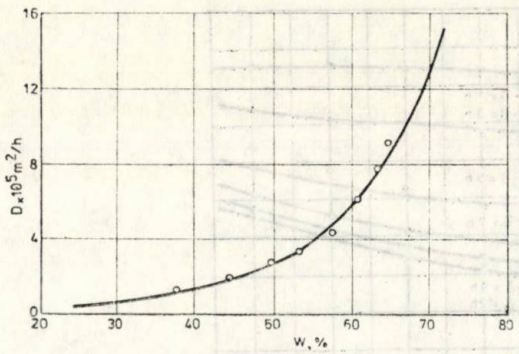


Fig. 5. — Variation of the coefficient of moisture migration as a function of material moisture.

By combining the equations (2) and (1) and using the finit differences one obtains :

$$D=\frac{1}{\Delta\tau}\cdot\frac{\int_0^x \Delta w\,dx}{\left(\frac{\partial w}{\partial x}\right)_x}= \tag{3}$$

$$=\frac{1}{\Delta\tau}\cdot\frac{\sum A_i}{\left(\frac{\partial w}{\partial x}\right)_x}.$$

In using the Eqs. (3), Δw and $\Delta\tau$ intervals are taken as small as possible so that the coefficient of moisture migration during the considered interval to be assumed constant. The A_i areas on the sample thickness are calculated, the amount of moisture shifted during the time interval $\Delta\tau$ through the cross section of sample being then obtained. Then the moisture gradient in the considered x position is determined and by means of Eq. (3) the value of moisture migration coefficient is calculated.

By using the moisture distribution curves given in Fig. 3 and the equation (3) the coefficient of moisture migration was calculated. The obtained results are plotted in Fig. 5 as variation of the moisture migration coefficient vs. the material moisture. The points in Fig. 5 represent the experimental values. Their disposition suggest an exponential equation for the coefficient of moisture migration. The equation derived for the variation of moisture coefficient is :

$$D=4.35\times10^{-7}e^{0.082w}. \tag{4}$$

The curve plotted in Fig. 5 corresponds to Eq. (4) which is valid for the layers of phenoxyacetic acid under the experimental conditions used. The coefficient of moisture migration was determined for the moisture values for which the concentration gradient could be calculated based on the curves of moisture distribution given in Fig. 3.

4. Discussion

Starting from the reason that the moisture migration in liquid state is an essential step in drying mechanism, a general drying model was advanced in literature, for the materials bathed on the surface by the drying agent [5] as well as two particular ones [2].

One of the particular models is obtained in case when the thickness of moisture migration zone is equal to the thickness of the material submitted to drying. This model is known as the model with complete zone of moisture migration or the model with two drying periods. The drying of phenoxyacetic acid bathed on the surface by the drying agent proceeds

according to this model. During the drying process two stages can be distinguished : the stage of formation of moisture migration zone, corresponding to the drying period constant rate and the stage of migration zone disappearance, corresponding to the period with decreasing rate.

During the period with constant rate the moisture migration takes place over whole thickness of material (Fig. 3) towards the surface where the evaporation proceeds. The moisture at the surface decreases until the equilibrium moisture is reached, after which the second period of drying, namely that with decreasing rate, begins. During this period the evaporation surface shifts within the material which determines the occurence of an additional resistance to the vapour diffusion. This fact diminishes the drying rate as the same time as the evaporation surface shifts towards inside the material. In this stage there are two zones within the material : the external dried zone and the internal one of moisture migration.

By studying the influence of temperature and air rate on the drying rate an increase of the latter with increasing parameters of the drying agent is noticed. A shift of the critical moisture towards higher values with increasing air parameters is also noticed. This fact can be accounted for by an increased moisture evaporation rate at the material surface compared to the rate of moisture evaporation from inside the material towards surface.

To obtain the curves of moisture distribution within the phenoxyacetic acid layers the gravimetrical method was used, the concentration gradient Δw being accomplished by evaporating the moisture from the material surface under the drying conditions. By means of the distribution curves the values of the coefficient of moisture migration through phenoxyacetic acid layers were determined.

Knowledge of the coefficient of moisture migration is particularly significant in elucidating the drying mechanism, as well as in estimating the drying duration, quite necessary for drier design. A high coefficient of moisture migration determines the shift of the critical point within the range of lower moistures which shortens the duration time.

5. Conclusions

The experimental results obtained in drying the phenoxyacetic acid allow the following conclusions to be drawn :

1. The drying process has two steages : a stage with a constant rate and another with a decreasing rate.

2. The increase of the parameters of the drying agent, such as temperature and flowing rate, determines an increase of the drying rate.

3. By using a gravimetrical method the curves of moisture distribution within the material were plotted. By means of these curves the coefficient of moisture migration was determined. For the experimental drying conditions used the coefficient of moisture migration was found to vary exponentially and an equation for its calculation was derived.

Notations

D — coefficient of moisture diffusion, [m²/s] ;
h — thickness of material, [m] ;

t — temperature, [°C];
U — drying rate, [Kg/m²h];
v — flowing rate of the drying agent, [m/s];
w — humidity, [%];
x — current length, [m];
τ — drying time, [h].

Received, October 8, 1981

Polytechnic Institute, Jassy,
Department of Chemical Engineering

REFERENCES

1. Tudose R., Cristian Gh., Patent R.S.R., *89 280* (1977).
2. Cristian Gh., *Studii de cinetica uscării cu aplicaţii la polimeri sintetici.* Ph. D. Diss., Polyt. Inst., Jassy, 1976.
3. Cristian Gh., Tudose R. Z., Rev. de Chimie, **27**, *10* (1976).
4. Căluianu V., *Contribuţii la studiul transferului de căldură şi masă în procesele de uscare ale materialelor ceramice.* Ph. D. Diss., Polyt. Inst., Buc., 1975.
5. Tudose R. Z., Cristian Gh., Bul. Inst. polit. Iaşi, **XXIII (XXVII)**, *1–2*, s. II (1977).

STUDII DE CINETICA USCĂRII ACIDULUI FENOXIACETIC

(Rezumat)

Sînt prezentate rezultatele experimentale obţinute în cazul uscării acidului fenoxiacetic prin trecerea agentului de uscare peste suprafaţa materialului. S-a studiat influenţa temperaturii şi vitezei aerului asupra vitezei de uscare. Experimental s-au obţinut curbele de distribuţie a umidităţii pe înălţimea materialului, pe baza cărora s-a determinat coeficientul de migrare a umidităţii. S-a stabilit o ecuaţie de calcul a coeficientului de migrare a umidităţii.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

C.D. 66.067 ; 546.131

PURIFICATION DE L'ACIDE CHLORHYDRIQUE TECHNIQUE DANS UNE INSTALLATION DESORBEUR—ABSORBEUR

PAR

ABDELKRIM AZZOUZ, M. MACOVEANU et IANCU HÂNCU

1. Introduction

Le but de ce travail consiste à appliquer un système désorbeur — absorbeur à la purification de l'acide chlorhydrique technique. À l'échelle pilote ce système fonctionne d'une façon discontinuelle ; les différentes opérations consistent en une désorption du gaz chlorhydrique jusqu'a une distillation azéotropique [1], [2] du résidu ; le gaz désorbé est entraîné par un courant d'azote et ensuite absorbé dans une colonne d'absorbtion et enfin concentré par recyclage. La phase suivante consiste à distiller au maximum le résidu afin de rentabiliser le procédé.

2. Expérimentation et description de l'appareillage

L'acide chlorhydrique technique est introduit dans un appareil à parois émaillé (Fig. 1) chauffé par un circuit d'huile chaude (chauffée par un circuit électrique). Le gaz chlorhydrique produit par désorbtion est refroidi par un condenseur, avant d'être introduit par le bas de la colonne d'absorbtion (du type E.I.V.S., France), entrainé par un courant d'azote.

Cette colonne a un garnissage avec des anneaux Raschig de porosité 0,68.

L'alimentation en solution absorbante (eau ou acide dilué à concentrer) s'effectue par le haut de la colonne et le système fonctionne ainsi à contrecourant. Les alimentations en gaz (bas) et en liquide (haut) sont contrôlées par déimètres manuels (*2*), deux prises de pression (*P*) et deux prises de températures (*T*) afin de contrôler respectivement le gradient de température et la perte de charge dans la colonne.

Le circuit de recyclage est constitué, quant à lui, par un recipient cylindrique, dit Bac-Tampon, d'une contenance de vingt litres, qui est relié à une pompe centrifuge.

Un débimètre et une prise de température (*T*) contrôlent l'entrée de l'absorbant dans la colonne.

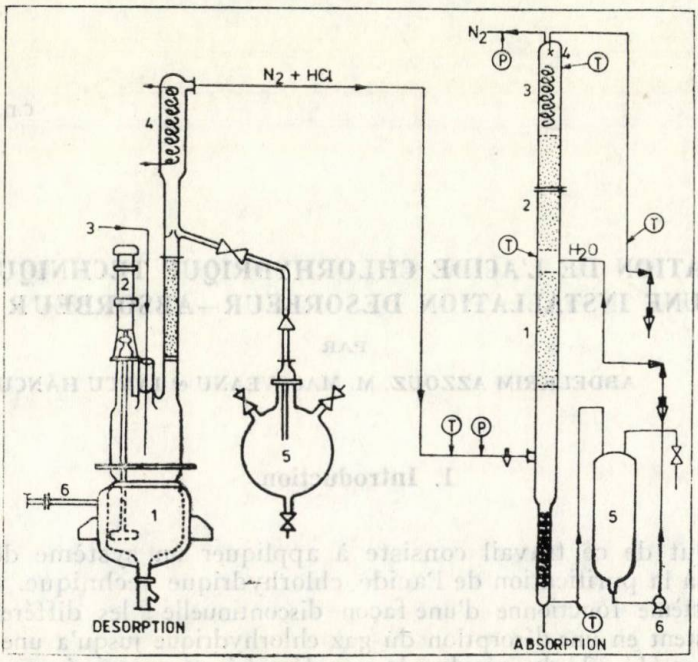


Fig. 1. — Description du système désorbeur—absorbeur. Partie désorbtion : *1* — désorbeur en acier vitré (bouilleur), *2* — moteur agitateur, *3* — alimentation azote, *4* — condenseur ; *5* — récupération distillat, *6* — circuit de chauffage à l'huile. Partie absorption : *1* — absorbeur isotherme, *2* — purificateur gaz reziduels (anneaux Raschig), *3* — condenseur, *4* — distributeur-liquide en croix, *5* — bac-tampon (circuit recyclage), *6* — pompe centrifuge.

Les gaz résiduels (azote et eventuellement HCl) sont purifiés par absorbtion dans une deuxième garnissage afin d'éviter tout risque de pollution.

3. Détermination des caractéristiques de la colonne d'absorption avec le système biphasique AIR—EAU [3]

Le volume total du garnissage est de 0,0173 m^3 dont 0,0071 m^3 pour la partie absorption isotherme (inférieure) et 0,0102 m^3 pour la partie purification des gaz résiduels (supérieure) (Fig. 1).

Le volume apparent de chaque anneau (verre+vide intracylindrique) est de $785{,}4 \cdot 10^{-9}$ m^3, d'où le nombre total d'anneaux Raschig de 22 000, ou à savoir $1{,}27 \cdot 10^6$ anneaux/m^3. Les parties inférieure et supérieure de la colonne possèdent respectivement 9 000 et 13 000 anneaux.

Le volume total de vide à l'intérieur des anneaux est de $621{,}72 \cdot 10^{-5}$ m^3 dont $254{,}34 \cdot 10^{-5}$ m^3 dans la partie inférieure. La surface de contact offerte par chaque anneau isolé est d'environ $6{,}03 \cdot 10^{-4}$ m^2.

La Fig. 2 présente la variation du débit d'air en fonction de la perte de charge entre le bas et le haut de la colonne (les deux garnissages y compris).

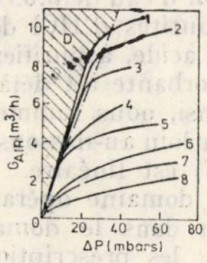


Fig. 2. — Détermination du domaine opératoire pour les débits liquides ($L_1 = 0$, $L_2 = 0{,}21$, $L_3 = 0{,}63$, $L_4 = 1{,}09$, $L_5 = 2$, $L_6 = 3$, $L_7 = 3{,}75$, $L_8 = 4$ l/h) pour le système air—eau à $T = 19°C$, $P = 1$ atm.; D — domaine opératoire.

On observe que pour de faibles débits liquides, la pente de la courbe $\Delta P = f(G_{air})$ [1], [3] est assez élevée; on peut assimiler cette courbe à une droite pour de faibles débits liquides (eau) et pour de faibles débits gazeux.

Le point de charge (*3*), correspondant au passage de l'état d'un mouillage incomplet à un bon mouillage, est assez difficile à déterminer, mais on peut toutefois localiser son domaine de présence (Fig. 2).

Le point d'engorgement (*3*), quant à lui, correspond au passage à l'état où le gaz ascendant forme un véritable obstacle au liquide descendent provoquant ainsi un bouillonement. Ce point s'interprète (Fig. 2) par une grande variation de la perte de charge pour une faible variation du débit gazeux, c'est-à-dire il correspond au début de la partie quasi-horizontale de la courbe $D_p = f(G)$.

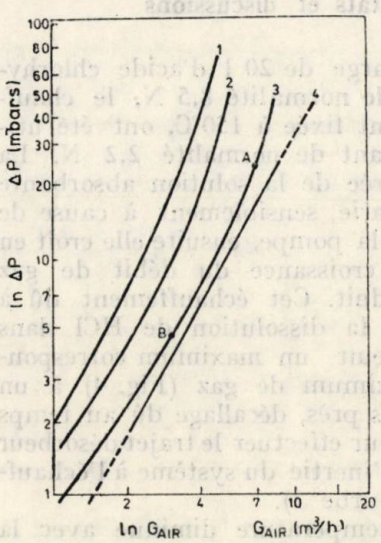


Fig. 3. — Détermination des points de charge et d'engorgement pour le système air—eau, pour un débit d'eau : $L_1 = 2$ m³/h, $L_2 = 1{,}09$ m³/h, $L_3 = 0{,}63$ m³/h, $L_4 = 0$ m³/h; A — point d'engorgement; B — point de charge; $T = 19°C$, $P = 1$ atm.

En coordonnées logarithmiques (relation de Sherwood, Shipler, Holloway et Bertelli et méthode de Lobo) [3], les points de charge et d'engorgement sont mieux répérables. La première partie de la courbe (Fig. 3) est analogue à celle obtenue pour un garnissage sec, mais avec une pente supérieure par suite de la diminution de la porosité et de l'augmentation des phénomènes de friction.

Ensuite la perte augmente sans variation visible de l'état de la colonne, par suite d'une retention de plus en plus grande de l'eau qui augmente la friction des gaz. Le point de brusque variation de la pente est dit point de charge (Loading Point). Dépassé ce point, la rétention de l'eau croit d'une façon linéaire et brusquement la pente de la courbe augmente encore une fois — c'est le point d'engorgement.

4. Détermination du domaine opératoire

Le gaz chlorhydrique étant très soluble dans l'eau [1], [4], la valeur d'un débit d'eau de 0,63 l/mn est déjà assez grande pour l'absorbtion de petites quantités d'HCl dont le débit excède rarement 1 m³/h pour une charge d'acide, à purifier, de 20 l de concentration 8,6 N, bien que la solution absorbante ait déjà une concentration initiale de 2,2 N.

Ainsi, nous sommes sûrs d'opérer avec de faibles débits d'eau et de gaz, donc loin au-dessous du point d'engorgement, c'est-à-dire là où la courbe $\Delta P = f(G)$ est linéaire.

Le domaine opératoire prescrit ($L \ll 1{,}5$ l/min et $G \ll 4$ m³/h) s'encadre bien dans le domaine opératoire D, déterminé expérimentalement (Fig. 2) ; les prescriptions préliminaires étaient d'opérer avec de faibles débits liquides ($L \ll 0{,}63$ l/min) pour de grands débits gazeux ; on peut aller jusqu'à des débits liquides de 2 l/mn.

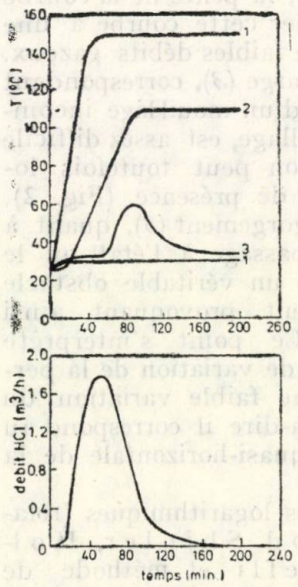


Fig. 4. — Variation de la température et du débit de HCl dans le temps : T_1 — température de l'huile chauffante, T_2 — température des vapeurs d'HCl (ou HCl — eau) dans le réacteur, T_3 — température de la sortie du dissolvant, T_4 — température d'entrée du dissolvant; charge : 20 l HCl (8,6 N) (désorbeur) ; dissolvant: 11,9 l HCl (2,2 N) (absorbeur) ; distillat obtenu : 5,5 l HCl ; résidu obtenu : 14,4 l HCl (6,33 N).

5. Résultats et discussions

Pour une charge de 20 l d'acide chlorhydrique technique de normalité 8,5 N, le chauffage de l'huile étant fixée à 150°C, ont été utilisés 12 l d'absorbant de normalité 2,2 N. La température d'entrée de la solution absorbante dans la colonne varie sensiblement à cause de l'échauffement de la pompe, ensuite elle croît en parallèle avec la croissance du débit de gaz chlorhydrique produit. Cet échauffement dû à l'exothermicité de la dissolution de HCl dans l'eau [5], [6], atteint un maximum correspondant au débit maximum de gaz (Fig. 4) à un intervalle de temps près, décallage dû au temps que met le gaz pour effectuer le trajet désorbeur —absorbeur et à l'inertie du système à l'échauffement (Fig. 4, courbe *3*).

Enfin cette température diminue avec la diminution du débit gazeux tendant vers la valeur initiale compte tenu du refroidissement. La température des vapeurs, quant à elle, croît très vite avec celle du chauffage (Fig. 4, courbes *2* et *1*) en parallèle avec la croissance de la pression partielle de HCl [7], avant de se stabiliser très vite aux environs de l'azéotrope (108°... 111°C).

Le débit gazeux commence à diminuer exactement avec l'augmentation de la pression partielle de l'eau, à cause du début de l'évaporation de l'eau et de la dissolution des vapeurs de HCl dans l'eau au niveau du

réfrigérant. De plus, la pression partielle de l'acide chlorhydrique, dans le bouilleur, diminue (Fig. 5 et 6) avec la diminution de la concentration de la charge [7]. À 110°C la charge bout comme un corps pur et à partir de ce moment-là la purification de l'acide chlorhydrique technique se produit exclusivement par distillation azéotropique (Fig. 6 et 7) dont le distillat est récupéré, ayant une concentration très voisine de celle du résidu (Fig. 5 et 6).

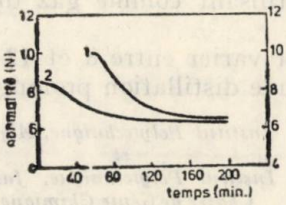


Fig. 5. — Variation des normalités dans le temps ; *1* — distillat; *2* — désorbeur (bouilleur).

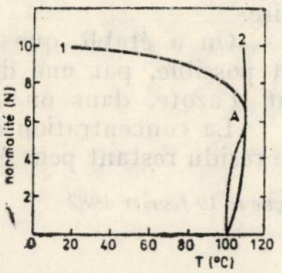


Fig. 6. — Variation des normalités en fonction de la température : *1* — désorbeur (bouilleur), *2* — distillat (condensation des vapeurs $HCl-H_2O$).

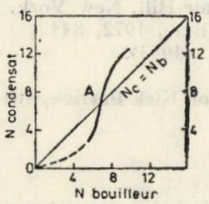


Fig. 7. — Variation de la normalité du distillat (condensat) en fonction de celle du bouilleur: *A* — point d'azéotrope négatif; $N_c = N_b = 6{,}3...6{,}5$ N(11,5% HCl) ; $T = 108...111$°C.

6. Conclusions

La valeur du débit de la solution absorbante n'ayant pas une grande importance, puisqu'il s'agit d'un circuit fermé, a été maintenue constante et possède une valeur respectant les normes prescrites préalablement.

Le résidu — ce qui est prévisible — a une normalité identique à celle de l'azéotrope. Au bout de 240 min d'opération, un acide de normalité 9 N désorbe (pendant les 200 premières minutes) 25 à 30% en poids de gaz et donne un distillat (25% en poids) de normalité 6,3...6,5 N (durant les 40 dernières minutes), dans notre installation.

La quantité de gaz désorbé croît linéairement avec celle de la charge pour une concentration fixée (constante de proportionalité variant entre 1/3 et 1/4) d'où l'on peut extrapoler et prévoir la quantité d'acide à absorber pour de grandes charges et la quantité d'absorbant, afin d'obtenir la concentration voulue, les pertes étant quasiment nulles dans cette installation.

Si la distillation azéotropique aurait été menée à terme, une grande quantité de distillat pouvait être produite.

Certes, nous avons obtenu des solutions (absorbant et distillat) de moindres concentrations, mais ces solutions peuvent servir à leur tour de solutions absorbantes afin d'y être concentrées, le but de ce travail étant de produire de l'acide chlorhydrique assez pur pour les besoins de laboratoire.

On a établi que la purification de l'acide chlorhydrique technique est possible, par une distillation azéotropique, utilisant comme gaz diluant l'azote, dans un appareil du type E.V.I.S.

La concentration de l'absorbant obtenu peut varier entre 8 et 12 N. Le résidu restant peut être à son tour purifié par une distillation prolongée.

Reçue le 19 fevrier 1982

Institut Polytechnique, Alger
et
Institut Polytechnique, Jassy,
Chaire de Génie Chimique

BIBLIOGRAPHIE

1. Norman W. S., *Absorption, Distillation and Cooling Towers*. Longmans, London, 1961.
2. Miranda M. A., Gaylord W. M., Chem. Eng. Progress, **53**, 3 (1957).
3. Treybal E. R., *Mass Transfer Operations*. Mc. Graw-Hill, New York, 1955.
4. * * * *Manualul inginerului chimist*. Vol. I, Ed. Tehn., Buc., 1972, 844.
5. Van Huys, Trans. Amer. Inst. Chem. Eng., **39**, 663 (1943).
6. Zeisberg K., Chem. a. Met. Eng., **32**, 326 (1925).
7. * * * *Perry's Chemical Engineer's Handbook*. Perry Chilton Kirk Patrick, 4th Ed., Mc. Graw-Hill, New York, 1967.

PURIFICAREA ACIDULUI CLORHIDRIC TEHNIC ÎNTR-O INSTALAȚIE DE DESORBȚIE–ABSORBȚIE

(Rezumat)

Au fost determinate condițiile de purificare pentru o soluție concentrată de acid clorhidric tehnic, prin distilare azeotropă și utilizarea azotului ca gaz diluant. Au fost stabilite de asemenea posibilitățile de obținere a soluțiilor de acid clorhidric cu concentrații ridicate.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

C.D. 547.821

PYRIDAZINIUM - YLURES (XII)

ACTION DU BROMURE DE *p.* MÉTHOXY-PHÉNACYLE SUR LA 3-PHÉNYLE-PYRIDAZINE

PAR

MARIA CAPROŞU, MARGARETA UNGUREANU et MAGDA PETROVANU

1. Introduction

Dans quelques travaux antérieurs [1]...[4] on a étudié les possibilités d'obtention de quelques dérivés pyridaziniques doués d'activités biologiques.

Dans le but d'obtenir de nouveaux dérivés pyridaziniques présentant une activité biologique, dans le présent travail on a étudié les possibilités de synthèse et la réactivité du 3-phényle-pyridazinium-(*p*.méthoxy)-phénacylure.

2. Résultats et discussions

Le 3 phényle-pyridazinium-(*p*.méthoxy)-phénacylure a été obtenu en utilisant la „méthode du sel". Ainsi, en traitant la 3-phényle-pyridazine (I) par le bromure de *p*.méthoxy-phénacyle (II) on obtient le bromure de N-(*p*.méthoxy)-phénacyle-3-phényle-pyridazinium (III). Par déhydrobromuration en milieu alcalin du sel de cycloimmonium (III) on obtient le 3-phényle-pyridazinium-(*p*.méthoxy)-phénacylure (IV) coloré en orange.

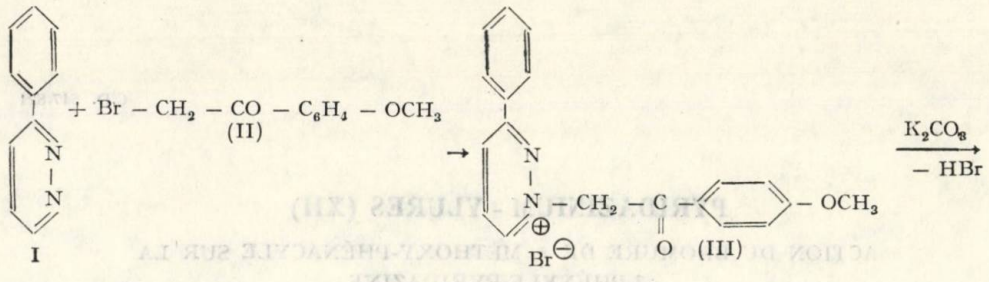
Cet ylure est assez stable, pouvant être conservé à l'abri de la lumière et de l'humidité une période assez longue de temps.

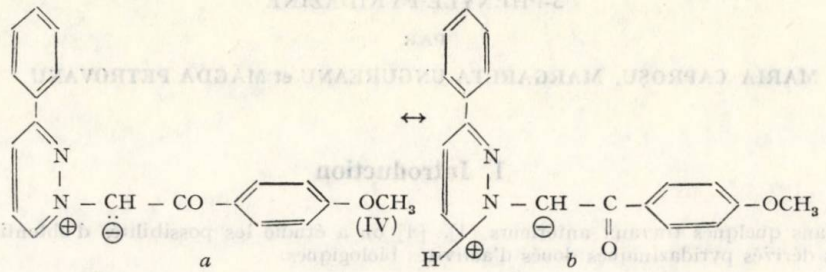
Grâce à sa structure de dipole 1,3 (IV *b*) le 3-phényle-pyridazinium-(*p*.méthoxy)-phénacylure peut participer à différentes réactions de cycloadditions 1,3 dipolaires avec divers dipolarophyles.

Ainsi, si l'on traite l'ylure (IV) obtenu *in situ* par l'acétylène dicarboxylate de méthyle on obtient l'ester diméthylique de l'acide 3-*p*-méthoxy-benzoyle-6-phényle-pyrrolino-[2, 1-b]-pyridazine-1,2-dicarboxylique (V).

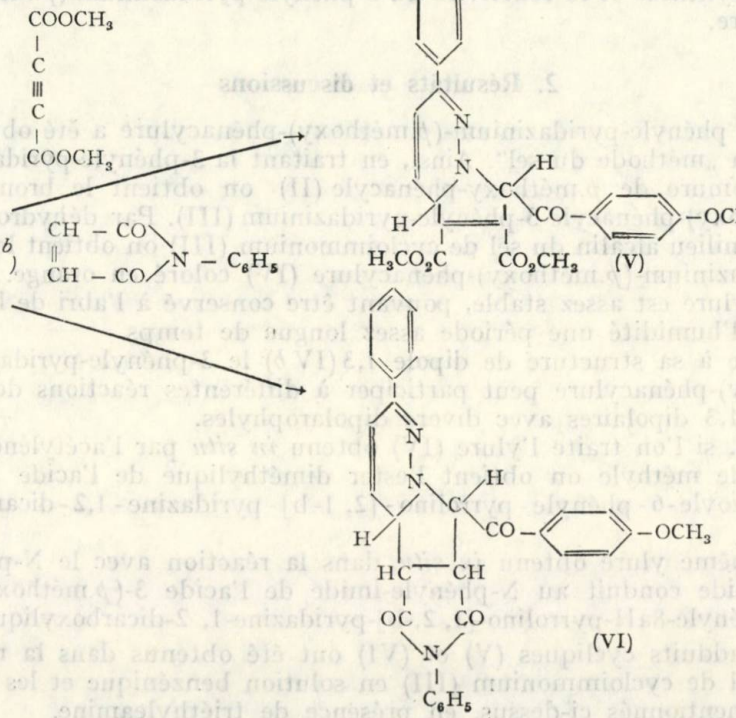
Le même ylure obtenu *in situ*, dans la réaction avec le N-phénylemaléine-imide conduit au N-phényle-imide de l'acide 3-(*p*.méthoxy)-benzoyle-6-phényle-8aH-pyrrolino-[1, 2,-b]-pyridazine-1, 2-dicarboxylique (VI).

Les adduits cycliques (V) et (VI) ont été obtenus dans la réaction entre le sel de cycloimmonium (III) en solution benzénique et les dipolarophyles mentionnés ci-dessus, en présence de triéthyleamine.


+ Br – CH2 – CO – C6H4 – OCH3
(II)
I
K2CO3
– HBr
(III)
Br⊖


OCH3
(IV)
a
b

(IV)


COOCH3
COOCH3
(IV b)
CH – CO
CH – CO
N – C6H5
H3CO2C
CO2CH2
(V)
OCH3
HC – CH
OC CO
N
C6H5
(VI)

Les structures des nouveaux produits obtenus ont été confirmées par les analyses chimiques et spectrales (IR).

3. Essais microbiologiques

Les nouveaux produits obtenus ont été testés du point de vue microbiologique afin de mettre en évidence une éventuelle activité antimicrobienne.

Le teste a été effectué en utilisant la méthode diffusiométrique avec des cylindres d'étain inoxydables, sur les microorganismes suivants : *Staphylococus aureus* Oxford, *Baccilus coli* Bruxelles et *Candida albicans*.

Les produits soumis aux testes ont été dissolus dans du diméthylsulphoxide et la détermination a été effectuée sur des Petri avec de la gélose pour les bactéries et en milieu Sabouraud pour *Candida albicans*.

Comme témoin on a utilisé le diméthylsulphoxyde qui a été le disolvant. Les plaques ont été maintenues 24 heures à 37°C. La lecture des résultats a été effectuée en mesurant le diamètre de la zone d'inhibition de la croissance des bactéries pour chaque produit à part, les valeurs étant exprimées en mm, comme on le voit dans le tableau 1.

Tableau 1

Souche	Produits testés			Témoin DMSO
	(III)	(IV)	(V)	
1. *Staphylococus aureus* Oxford	23 mm	12 mm	0 mm	0 mm
2. *Baccilus coli* Bruxelles	12 mm	19 mm	12 mm	17 mm
3. *Candida albicans*	25 mm	12 mm	12 mm	10 mm

L'analyse des données inscrites dans le tableau 1 montre que l'activité la plus importante est manifestée par le sel de cycloimmonium (III). Ainsi, le sel est actif envers le *Staphylococus aureus* Oxford (23 mm) et envers *Candida albicans* (25 mm).

3. Partie expérimentale

a) *Bromure de N-p. méthoxy-phénacyle-3-phényle-pyridazinium (III)*

On dissout 1,5 g (0,01 mol) de 3 phénylè-pyridazine dans 30 ml alcoole méthylique absolu et on ajoute une solution de 2,29 g (0,01 ml) bromure de *p*-méthoxy-phénacyle dans 20 ml d'alcoole méthylique absolu. On mélange les deux solutions et on porte à reflux pendant 3 h. Après le refroidissement de la solution on précipite le sel avec de l'éther éthylique. Cristaux blancs à p.f. 211°C.

Analyse : $C_{19}H_{17}N_2O_2Br$

	C%	H%	N%
Calculé :	59,22	4,41	6,23
Trouvé :	59,51	4,63	6,40

Spectre IR(KBr) : ν_{CO} = 1 702 cm^{-1} ; $\nu_{C=C}$ = 1 603, 1 590, 1 574 cm^{-1}.

b) *3-Phényle-pyridazinium-p. méthoxy-phénacylure (IV)*

On dissout 3,85 g (0,01 mol) de bromure de N-*p.* méthoxy-phénacyle-3-phényle-pyridazinium dans 50 ml d'eau et on ajoute, goutte, à goutte une solution de 1,38 g(0,01 mol) K_2CO_3 dans 20 ml d'eau. Il se forme un précipité orange qu'on filtre et lave avec de l'eau jusqu'à pH neutre. On recristallise dans du benzène. P.f. 128°C.

Analyse : $C_{19}H_{16}O_2N_2$

	C%	H%	N%
Calculé :	75,00	5,26	9,21
Trouvé :	75,52	5,60	9,52

c) *N-phényle-imide de l'acide-3-méthoxy-benzoyle-9H-pyrrolino-[2,1b]-6-phényle-pyridazine 1,2-dicarboxylique (V)*

On dissout 3,85 g(0,01 mol) de bromure de N-*p.*méthoxy-phénacyle-pyridazinium dans 40 ml benzène, on ajoute 1,73 g (0,01 mol) de triéthyle-amine, on porte à reflux le mélange pendant 4 h. On filtre la solution bouillante afin d'éliminer le bromhydrate de triéthyle-amine. Il se sépare du filtrat, en refroidissant, un produit banc-jauneâtre à p.f. 120°C.

Analyse : $C_{25}H_{22}N_2O_6$

	C%	H%	N%
Calculé :	72,95	4,82	8,80
Trouvé :	73,40	5,30	9,12

d) *1,2-Dicarbométhoxy-3 p.méthoxy-benzoyle-3,9-dihydropyrrolo-[2,1b]-6-phényle-pyridazine (VI)*

On suspend 3,85 g (0,01 mol) de bromure de N-*p.*méthoxy-phénacyle-3-phényle-pyridazinium dans 50 ml benzène, on ajoute 1,42 ml (0,01 mol) acéthylènedicarboxylate de méthyle et 1,4 ml (0,01 mol) de triéthyle-amine. On porte à reflux le mélange pendant 4 h. On filtre la solution bouillante afin d'éliminer le bromhydrate de la triéthyle-amine. En refroidissant le filtrat on obtient un produit jaune foncé à p.f. 101°C.

Analyse : $C_{25}H_{22}N_2O_6$

	C%	H%
Calculé :	67,26	4,93
Trouvé :	67,52	4,74

Spectre IR(KBr) : $\nu_{CO^{e}ster.} = 1\,740\ cm^{-1}$, $\nu_{C=Ocet.} = 1\,693\ cm^{-1}$, $\nu_{C-O-C} = 1\,237$, 1 203, 1 170 cm^{-1} ; $\nu_{\varphi-H} = 870$, 830, 770, 750 cm^{-1}.

Reçue le 17 mai 1982

Institut polytechnique, Jassy,
Chaire de Chimie organique et macromoléculaire

BIBLIOGRAPHIE

1. Ştefănescu E., Petrovanu M., Rev. Med. Chirurg., Iaşi, **LXXXI**, 2, 291 (1977),.
2. Ştefănescu E., Caproşu M., Gafiţanu E., Dăneţ R., Petrovanu M. Rev. Med. Chirurg., Iaşi, **LXXXIII**, 2, 311 (1979).
3. Caproşu M., Ungureanu M., Druţă I., Stavri N., Petrovanu M., Bul. Inst. polit. Iaşi, **XXV (XXIX)** *1–2*, s. II, 79 (1979).
4. Petrovanu M., Caproşu M., Ungureanu M., Stavri N., Rev. Med. Chirurg. Iaşi, **LXXXIV**, *3*, 507 (1980).

PIRIDAZINIU - ILIDE

XII. Acţiunea bromurii de *p*-metoxi-fenacil asupra 3-fenil-piridazinei

(Rezumat)

În continuarea cercetărilor privind obţinerea diaziniu-ilidelor, se descrie sinteza a patru produşi noi, derivaţi ai 3-fenil-piridazinei, a căror structură a fost confirmată pe baza analizelor chimice şi spectrale.

S-a testat, de asemenea, activitatea antimicrobiană a produşilor noi studiaţi.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secția II
CHIMIE și INGINERIE CHIMICĂ

D.C. 539.153 : 547.564.3 : 547.854.5

ON THE CHARGE TRANSFER ELECTRONIC SPECTRA OF THE COMPOUNDS OBTAINED FROM NEUTRAL RED AND PICRIC ACID, BARBITURIC ACID, PHENOBARBITAL

BY

I. COCÎRLĂ, C. I. GHIRVU and LUMINIȚA PĂUNESCU

1. Introduction

It is well known [1], the charge transfer transitions may be considered to have the origin into the following process:

$$D + A \rightleftharpoons (DA)_{\text{compl.}} \overset{h\nu}{\rightleftharpoons} (DA)^*_{\text{compl.}}$$

where D is the electron donor and A — the electron acceptor, (DA) — the complex and $(DA)^*$ — the electronic excited state of the complex, resulted as effect of the absorption. Usually, the electronic transition of the lowest energy correspond to the transfer of an electron from the highest occupied molecular orbital of donor (HOMO) to the lowest unoccupied molecular orbital of acceptor (LUMO). Certainly, supplementary bands could appear, as effect of other possible transitions from the molecular orbitals of D to the molecular orbitals of A, however, these bands are overlapped by those of D or A. The charge transfer bands (CT) can be recognized as having no vibrational structure, rather they are generally very broad featureless bands due to the numerous possible spatial orientations of D and A [2].

It has been found empirically the frequency, ν_{CT}, of charge transfer bands by, the relation [3]:

$$h\nu_{CT} = I_D - E_A + \Delta, \tag{1}$$

where I_D is the ionization potential of the donor, E_A — the electron affinity of the acceptor, and Δ — a constant for a related serie of donors.

In this paper, the electronic spectra (in UV—VIS) of some molecular complexes obtained from neutral red and organic compounds have been investigated. The energies of bands for the HOMO—LUMO transition were correlated with data obtained from the Hückel OM type calculations [4].

2. Experimental

Neutral red behave like a cation in aqueous solution. It reaction with compounds, that in similar conditions can function like anions. On this purpose, some organic compounds was used, presenting voluminous anions (picric acid, barbituric acid, phenobarbital). The separation of corresponding derivatives with neutral red is practically immediate.

It was used aqueous solutions 10^{-1} M for the both partners, the working medium beeing acid (pH≈1), exception the compound formed with phenobarbital (pH=6...7).

The obtained precipitates were filtred, washed with water, a little amount of alcohol and ether. Then, its was dried at vacuum (room temperature). The analysis results agree with the calculated ones, confirming the combination ratio phenazinic derivative : complexation anion, for the obtained compounds [5].

The products are insoluble in water, chloroform (exception those with medicines), ethyl ether, carbon tetrachloride, benzene, nitrobenzene, *n*-butyl alcohol, isopropyl alcohol, butyl acetate, soluble in 1, 2-dichlorethane, acetone (only those of medicines), methyl-ethyl cetone, cyclohexanone, very soluble in ethyl and methyl alcohols (only those of medicamentous substances, the others soluble), propylene glycol, DMSO, DMF and dioxan.

3. Calculation Method and Parameters

The energy levels and wave functions were obtained by H ü c k e l OM type calculation [4] for molecular systems (Fig. 1).

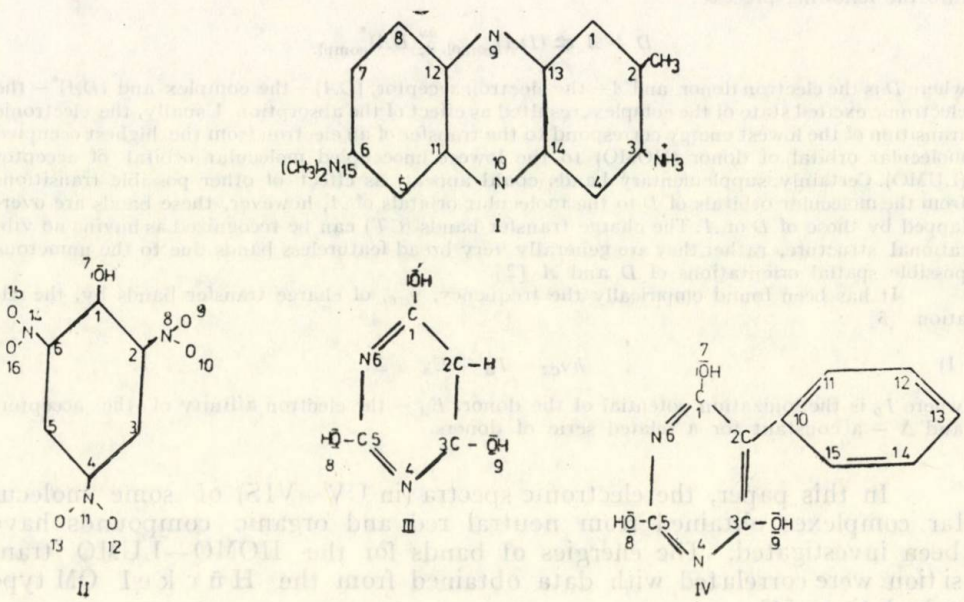


Fig. 1. — The notation of atoms for molecular systems : *I* — neutral red ; *II* — picric acid ; *III* — barbituric acid ; *IV* — phenobarbital.

The following parameters were used [6] :

$$\alpha_N=\alpha+0.5\beta\ ;\ \alpha_{\ddot{N}}=\alpha+1.1\beta\ ;\ \alpha_{OH}=\alpha+1.8\beta\ ;\ \alpha_{N(nitro)}=\alpha+1.7\beta\ ;$$

$$\alpha_{O(nitro)}=\alpha+0.4\beta\ ;\ \alpha_{C-\ddot{N}}=0.8\beta\ ;\ \beta_{C-OH}=0.7\beta\ ;$$

$$\beta_{C-N(nitro)}=0.6\beta\ ;\ \beta_{N-O}=0.9\beta\ ;\ \beta_{C-C_6H_5}=0.9\beta.$$

For the molecule I, the CH_3 and $\overset{+}{N}H_3$ groups were considerated only by their inductive effects, using the corresponding parameters $\alpha_2=\alpha+0.5\beta$; $\alpha_3=\alpha-0.2\beta$.

4. Results and Discussions

The obtained data in UV—VIS spectra for the considerated molecules and their corresponding complexes are presented in Table 1.

Table 1

The Obtained Transition Energies for Investigated Systems

Molecule	Transition energies eV				
	λ_1	λ_2	λ_3	λ_4	λ_5
I (donor)	4.87	4.37	2.82*)	2.34	—
II (acceptor)	4.74	4.32	3.65	2.95	—
III (acceptor)	4.85	3.65	—	—	—
IV (acceptor)	4.83	3.46	—	—	—
(I+II) complex	4.77	4.42	3.54	2.85	2.30**)
(I+III) complex	4.74	4.28	3.62**)	2.22	—
(I+IV) complex	4.92	4.45	3.79**)	2.89	—

*) shoulders ; **) bands assumed of charge transfer type.

In Table 2 Hückel MO results for the energies of the highest occupied molecular orbitals of donor and the lowest unoccupied ones of acceptor, as well as their difference are given.

Table 2

The Results of MO Calculation

Molecule	Energies (β)		
	E_{HOMO}	E_{LUMO}	$\Delta E=E_{LUMO}-E_{HOMO}$
I	0.5019	−0.2089	−0.7108
II	0.4000	−0.3424	−0.7424
III	0.8639	−0.8973	−1.7612
IV	0.6299	−0.7767	−1.4066

To calculate the transition energies of charge transfer bands, we used an internal parametrization method for limited configurational interaction calculations [7], [8]. So, it was considered as internal etalon the complex (I + II), for which the transition energy due to the band localized at the longest wavelength (charge transfer band (*CT*)) is 2.30 eV (s. Table 1). This energy was equalized with that obtained as result of the electronic transition from HOMO (donor) to LUMO (acceptor), and a particular value for the corresponding β ($\beta = -2.724$ eV) was obtained. This value was used to calculate the transition energies corresponding to charge transfer bands of the other two complexes. The obtained data and their comparison with the experimental values are presented in Table 3.

Table 3

Transition Energies Corresponding to Charge Transfer Bands and their Comparison with Experimental Values

Complex	$\frac{\Delta E_{CT} = E_{LUMO} - E_{HOMO}}{\beta}$	E_{CT}, [eV] $\beta = -2.724$ eV	ΔE_{CT}, [eV] Experimental value
(I + II)	−0.8443	2.30	2.30
(I + III)	−1.3992	3.81	3.62
(I + IV)	−1.2786	3.48	3.79

From this table it can be observed a satisfactory agreement between the calculated and the experimental values, assumed to the transition energies of the charge transfer bands.

5. Conclusions

We can conclude that the electronic spectra of the studied complexes contain both bands corresponding to electronic transitions between separated energy levels of acceptor and donor respectively, and charge transfer bands. This observation is also supported by the energies of the HOMO —LUMO transitions of donors, that are comparable or even smaller than those corresponding to HOMO (donor)—LUMO (acceptor), as it can be seen in Tables 2 and 3.

Received, April 8, 1982

Polytechnic Insitute, Jassy,
Department of Organic and Macromolecular Chemistry
and
Department of Inorganic, and Analytical Chemistry

REFERENCES

1. Mulliken R. S., Pearson W. B., *Physical Chemistry. An Advanced Treatice.* Ed. H. Eyring, D. Henderson, W. Jost, vol. III, Acad. Press, New York — London, 1969, 537.

2. Brittain E. F. H., George W. O., Wells C. H. J., *Introduction to Molecular Spectroscopy Theory and Experiment*. Acad. Press, London — New York, 1970, 57.
3. Suzuki H., *Electronic Absorption Spectra and Geometry of Organic Molecules*. Acad. Press, New York — London, 1967.
4. Hückel E., Z. Phys., **70**, 204 (1931); Ibid., **76**, 628 (1932).
5. Păunescu L., *Reactivi din grupa fenazinei*. Ph. D. Diss., Polyt. Inst., Jassy, 1981.
6. Fișel S., Păunescu L., Bul. Inst. polit., Iași, **XXVII (XXXI)**, *1—2*, s. II, 23 (1981).
7. Purcell W. P., Singer J. A., J. Chem. Eng. Data, **12**, 235 (1967).
8. Cocârlă I., Ghirvu C. I., Bul. Inst. polit., Iași, **XXIII (XXVII)**, *3 — 4*, s. II, 69 (1977).
9. Ghirvu C., Strat G., Strat M., An. șt. Univ. „Al. I. Cuza", Iași, (serie nouă), **XXVII**, s. I, Fizică, 45 (1981).

ASUPRA SPECTRELOR ELECTRONICE CU TRANSFER DE SARCINĂ ALE COMPUȘILOR OBȚINUȚI DIN ROȘU NEUTRU ȘI ACID PICRIC, ACID BARBITURIC, FENOBARBITAL

(Rezumat)

Spectrele electronice în (UV—VIS) ale unor complecși moleculari obținuți din roșu neutru și compuși organici (acid picric, acid barbituric, fenobarbital) au fost investigate. Energiile benzilor pentru HOMO (orbitalul molecular ocupat cel mai înalt al donorului) —LUMO (orbitalul molecular neocupat cel mai jos al acceptorului) au fost corelate cu datele obținute din calculele OM tip Hückel. S-a conchis că spectrele electronice ale complecșilor considerați conțin atît benzi corespunzînd tranzițiilor electronice între nivelele energetice ale acceptornlui și donorului, cît și benzi de transfer de sarcină.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

C.D. 541.128 ; 547.625

ÉTUDES SUR LA SÉLÉCTIVITÉ DES CATALYSEURS POLYFONCTIONNELS DANS LE PROCESSUS DE DISPROPORTIONATION DU TOLUÈNE

PAR

SPIRIDON OPREA, EMIL DUMITRIU, MARIANA STRUGARIU et ABDELKRIM AZZOUZ

1. Introduction

La production du benzène a connu un développement continu et rapide sur plan mondial, grâce à son utilisation comme matière première dans la fabrication de nombreux produits chimiques importants á savoir: matières plastiques, caoutchoucs synthétiques, fibres synthétiques, détergents, médicaments, etc. Il en fut de même pour ce qui concerne la production des xylènes qui, quant à eux, sont utilisés dans des domaines importants comme celui des fibres synthétiques, résines, laques, plastifiants, etc. Par contre, le toluène, qui s'obtient avec le benzène et les xylènes de la fraction BTX résultant des processus de reforming catalytique des essences et de pirolyse des fractions pétrolières, présente pour le moment des domaines d'application restreints. Par conséquent, la situation de la production et de la consommation des benzènes, toluènes et xylènes se caractérise par une grande consommation de benzène et xylènes et un excédent de toluène.

L'application de certains procédés comme l'hydrodéalkylation ou, plus récemment, la disproportionation et la transalkylation, résoud le problème de cet excédent. Les deux derniers procédés présentent des indices techniques et économiques plus avantageux. De plus, ces procédés possèdent aussi un caractère de flexibilité ; si la demande en benzène est plus grande la disproportionation s'avère plus adéquate, tandis que si les demandes en *orto*- et *para*-xylène sont en croissance, ces procédés industriels ont recours au procéssus de transalkylation.

Grâce à l'importance que présente la valorification supérieure du toluène dans l'obtention du benzène et des xylènes par les procédés de disproportionation et transalkylation, certaines études ont été initiées, portant sur les réactions principales sur lesquelles se basent ces procédés. De même, il faut rappeler que dans ce processus divers catalyseurs ont été testés, à savoir ; aluminosilicates naturels et synthétiques, catalyseurs du type Friedel-Crafts; mais les meilleurs résultats ont été obtenus sur des zéolithes synthétiques [1]...[3].

Dans le cadre de cette classe de catalyseurs, on peut citer les zéolithes du type faujasite X et Y, mordenites, les clinoptiolithes et érionites, sous forme Na, H ou avec divers cations métalliques introduits par échange ionique.

Le présent travail se propose d'étudier un catalyseur du type CeLaY, partant des considérations que les deux cations augmentent l'activité catalytique ; en même temps la sélectivité de la disproportionation est favorisée par l'intermédiaire du Lanthane.

2. Partie expérimentale

L'installation expérimentale du procédé de disproportionation du toluène en benzène et xylènes (Fig. 1) a comme élément principal un réacteur différentiel (*9*) réalisé en verre et chauffé par un système composé

d'un bloc métallique et de deux résistances électriques alimentées par un autotransformateur variable. La température à l'intérieur du réacteur, au milieu de la couche de catalyseur, a été mesurée à l'aide d'un thermocouple Chromel—Alumel.

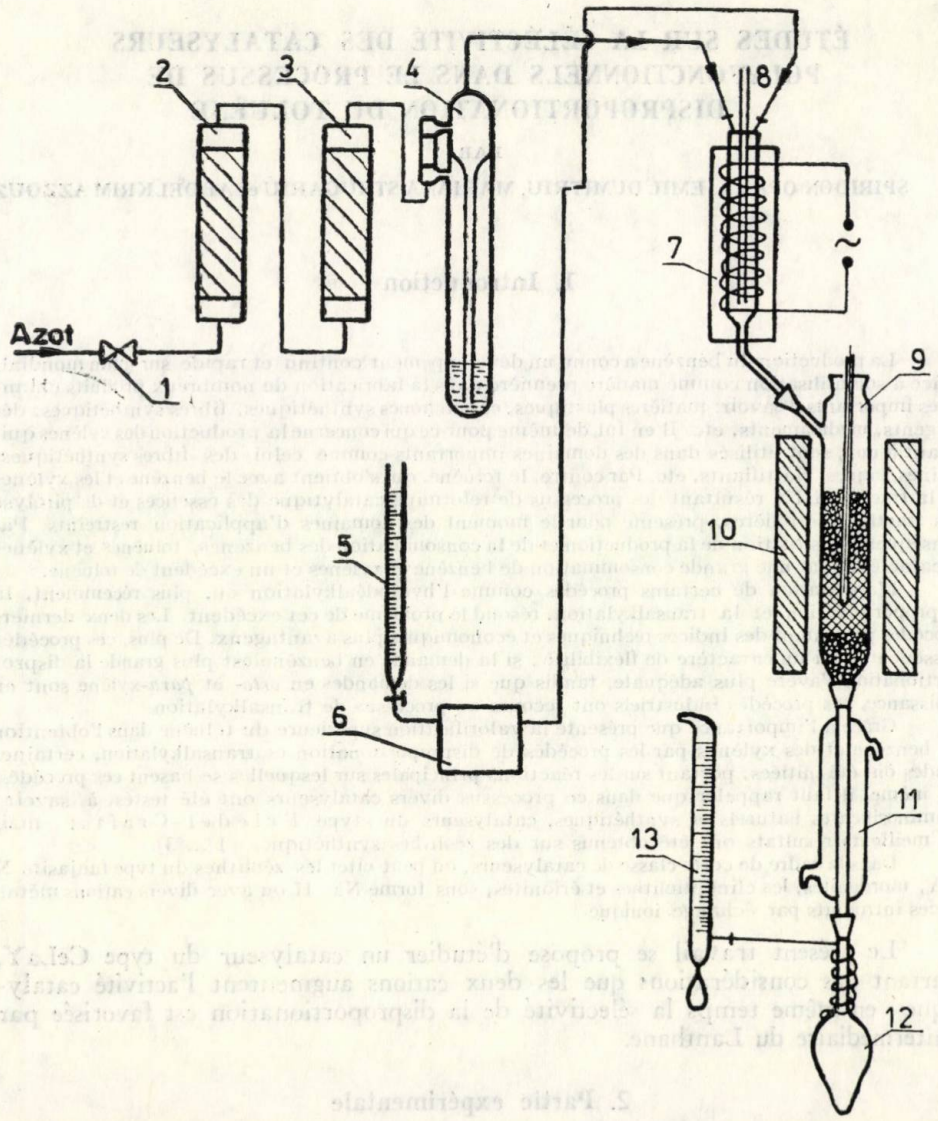


Fig. 1. — Schéma de l'installation de disproportionation du toluène : *1* — robinet ; *2, 3* — vases de séchage ; *4* — débimetre capillaire ; *5* — burette ; *6* — pompe dozeuse ; *7* — évaporateur ; *8* — thermomètre ; *9* — réacteur ; *10* — bloc métallique de chauffage ; *11* — refrigérant ; *12* — trappe collecteuse ; *13* — débimetre à film de savon.

Le catalyseur, en quantité de 3,27 g, a été introduit dans la zone centrale du réacteur entre deux couches de billes de verre. La granulation de ce catalyseur—entre 1 et 2 mm. L'évaporateur (*8*), réalisé en verre, est chauffé par l'intermédiaire d'une résistance électrique et la température est mesurée par un thermomètre. Le toluène est introduit dans l'évaporateur par l'intérmediaire d'une burette (*5*) et de la pompe dozeuse (*6*). L'azote a été utilisé comme gaz porteur. Les produits de réaction sont récupérés dans un récipient refroidi à la glace.

L'analyse des produits de réaction s'est effectuée dans un chromatographe CHROM 42,muni d'un détecteur à ionisation de flamme. La colonne chromatographique a un diamètre intérieur de 4 mm et une longueur de 2,7 m. Le garnissage est assuré par du Chromosorb W avec 3% de DC 200. L'azote joue le rôle de gaz porteur.

Préalablement le toluène a été fractionné et la fraction du milieu a été collectée et analysée chromatographiquement. L'hydrogène et l'azote ont été débarassés des traces d'eau. Le catalyseur utilisé avait un degré d'échange cationique de 81,75%.

3. Résultats et discussions

Selon la littérature de spécialité [3], les zéolithes présentent une activité catalytique dans le domaine de température 350°...500°C, dans le processus de disproportionation. Tenant compte de ce fait, la première étape de notre étude a porté sur l'observation du comportement de l'activité du catalyseur CeLaY dans le domaine 400°...460°C.

À partir de la Fig. 2 on remarque que l'activité du catalyseur enregistre un maximum à la température de 440°C. De plus, l'analyse des produits de réaction a permis de constater qu'au-delà de 440°C la proportion des produits polysubstitués croît.

Il est évident que l'analyse de l'activité du catalyseur dans le temps présente un intérêt particulier. Les tests de laboratoire effectués ont montré qu'en général, après environ 40 min., l'activité du catalyseur décroît progressivement. Ce fait a été interprété par la formation du cock et à un degré moindre comme conséquence de l'empoisonnement du catalyseur. L'hypothèse a été vérifiée par la combustion du cock en courant d'air et les données expérimentales ont prouvé que l'activité initiale élevée du catalyseur se maintient au même niveau.

Pour la stabilité des conditions expérimentales et pour assurer une bonne reproductibilité, un intervalle de 30 min. a été choisi comme domaine de temps.

Il faut mentionner, pour une éventuelle réalisation technologique, que la diminution de l'activité catalytique dans le temps constitue un facteur extrêmement important car, comme on le remarque dans la Fig. 3, simultanément avec la chute de l'activité a lieu aussi une chute considérable de la sélectivité du catalyseur.

Par la suite, l'étude a porté sur l'influence de la température et de la vitesse spatiale sur la sélectivité et le rapport B/X (benzène/xylènes).

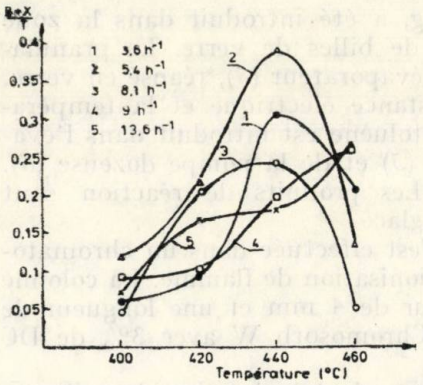


Fig. 2. — Variation de la conversion en fonction de la température à différentes vitesses spatiales : *1* — 23,6 h^{-1} ; *2* — 5,4 h^{-1} ; *3* — 8,1 h^{-1} ; *4* — 9 h^{-1} ; *5* — 13,6 h^{-1}.

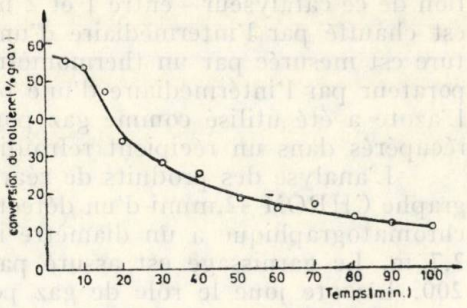


Fig. 3. — Variation de la sélectivité du catalyseur dans le temps.

Ainsi, dans la Fig. 4 est représentée la variation du rapport B/X en fonction de la température pour différentes vitesses spatiales. De ce graphique on remarque qu'aux vitesses spatiales comprises entre 5 et 9 h^{-1}, le rapport B/X se maintient autour de la valeur 1 pour le domaine de température 420°...440°C. À la température de 460°C la valeur du rapport B/X descend sous l'unité.

Des conclusions similaires s'obtiennent aussi pour l'étude de l'influence de la température sur la sélectivité, à différentes vitesses spatiales (Fig. 5). Il est évident qu'à la température de 440°C la sélectivité est optimale pour des vitesses spatiales comprises entre 3,6 et 8,1 h^{-1} ; pour des vitesses spatiales plus grandes, la sélectivité croît avec la température.

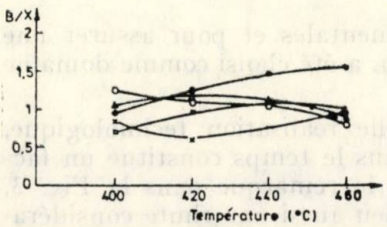


Fig. 4. — Variation du rapport B/X en fonction de la température à différentes vitesses spatiales.

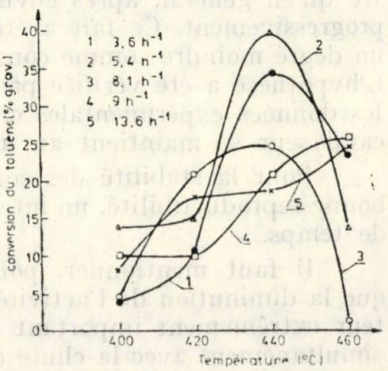


Fig. 5. — Variation de la sélectivité avec la température à différentes vitesses spatiales.

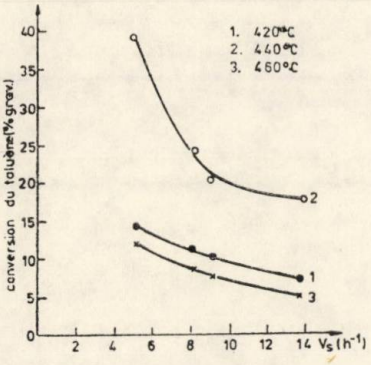


Fig. 6. — Variation de la conversion en fonction de la vitesse spatiale à différentes températures.

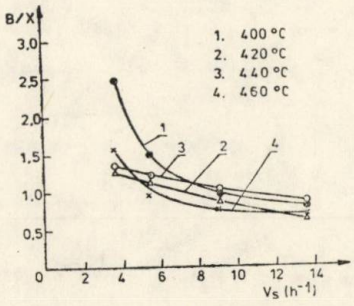


Fig. 7. — Dépendance du rapport B/X de la vitesse spatiale.

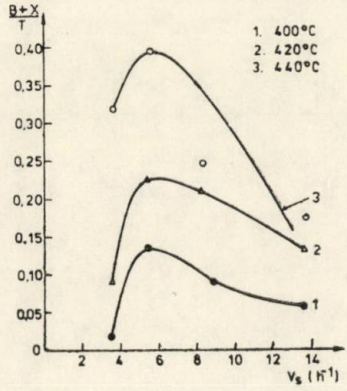


Fig. 8. — Variation de la sélectivité avec la vitesse spatiale.

Le facteur suivant ayant été analysé fut l'influence de la vitesse spatiale. Dans la Fig. 6 est représentée la variation de la conversion en fonction de la vitesse spatiale. Il a été permis de remarquer, comme l'on devait s'y attendre, la chute de la conversion avec l'augmentation de la vitesse spatiale ; mais pour les valeurs de température de 460° et 420°C la chute est plus lente dans le temps, tandis que pour la valeur de 440°C elle est beaucoup plus rapide. De même, le rapport B/X est influencé par la vitesse spatiale. La Fig. 7 montre que le rapport B/X décroît avec l'augmentation de la vitesse spatiale. Cela pourrait s'expliquer par la présence du processus de formation des hydrocarbures polysubstitués, qui est due au temps de réaction plus élevé.

Enfin, l'étude s'est orientée vers l'influence de la vitesse spatiale sur la sélectivité (Fig. 8). La sélectivité maximum s'obtient pour une vitesse spatiale de 5,4 h^{-1}, donc la sélectivité croît de la valeur de la vitesse spatiale de 3,6 h^{-1} à la valeur de 5,4 h^{-1}, valeur après laquelle on constate une chute progressive de la sélectivité. De même que pour le cas précédent, pour la température considérée optimum, à savoir 440°C, la chute de la sélectivité a lieu beaucoup plus rapidement avec l'augmentation de la vitesse spatiale.

4. Conclusions

L'étude effectuée met en évidence le fait que la faujasite Y, où les ions Na^+ ont été remplacés par le Cerium et le Lanthane, présente une activité particulière. Il est permis d'affirmer que pour le catalyseur fraîchement activé la conversion maximum thermodynamiquement possible est atteinte approximativement, observation qu'on n'a pas rencontré jusqu'à présent dans la littérature de spécialité. Cet aspect ne peut pas conduire qu'à la conclusion de l'opportunité de continuer les études dans la direction initiale.

Relativement à la présente étude deux aspects importants peuvent être mis en évidence : d'abord le fait que la température optimum est de 440°C, ce qui signifie que des températures plus élévées ne sont pas nécessaires ; de plus, cette température coïncide avec la température utilisée dans le procédé industriel TATORAY [2].

L'autre aspect est lié au fait que la vitesse spatiale de 5,4 h^{-1} est optimum pour le processus étudié ; par conséquent le processus pourrait être réalisé dans des conditions relativement modérées du point de vue énergétique.

Reçue le 4 novembre 1981

Institut Polytechnique, Jassy,
Chaire de Chimie organique et macromoléculaire
et
Institut Polytechnique, Alger

BIBLIOGRAPHIE

1. Aneke L. E., Gerritsen L. A., Eilers J., Trion R., J. Catalysis, **59**, 37 (1979).
2. Iwamura T., Otani S., Sato M., Bull. Jap. Petr. Inst., **13**, 1 (1971).
3. Goidea N., Goidea D., Șerban G., Rev. Chim. (Buc.), **7**, 497 (1973).

STUDII PRIVIND SELECTIVITATEA CATALIZATORILOR POLIFUNCȚIONALI ÎN PROCESUL DE DISPROPORȚIONARE A TOLUENULUI

(Rezumat)

S-a studiat reacția de disproporționare a toluenului pe un catalizator de tip faiazit Y, în care ionii de sodiu au fost schimbați cu ioni de ceriu și lantan. S-a urmărit influența diferiților factori (temperatură, viteză spațială etc.) asupra conversiei și selectivității. Se constată că cele mai bune rezultate se obțin pentru viteza spațială de 5,4 h^{-1} și temperatura de 440°C.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV). Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

УДК 678.053

МЕХАНОХИМИЧЕСКИЙ СИНТЕЗ ВЫСОКОМОЛЕКУЛЯРНЫХ СОЕДИНЕНИЙ

КЛЕОПАТРА ВАСИЛИУ-ОПРЕА

1. Введение

Механическое превращение является результатом сосредотачивания упругой энергии в объёмах малого значения или в тонких поверхностных слоях, согласно специфичным механизмам. Но в большинстве случаев протиканию способствуют и многочисленные другие эффекты, которые развиваются одновременно и неотвратимо : большие температуры и давления, сильные электризации, электронные потоки, сопуствующие им магнитные поля, чередование и действие которых происходит чрезвычайно быстро из-за малых значений размеров и продолжительностей существования областей местного максимального сосредотачивания механической энергии, а именно, радиусов порядка $10^{-3}...10^{-7}$ см и, соответственно, продолжительностей порядка $10^{-3}...10^{-6}$ сек.

Энергия, выделённая в таких условиях (под действием ударных волн, при трении, и.т.п.) обуславливает—вследствие малой теплопроводности полимеров—не только местные перегревы, но и „микровзрывы", которые способствуют переходу их в новое состояние, в состояние плазмы, состоящей из ионов, радикалов, электронов, и.т.п., которое объясняет многообразие химических реакций.

В дальнейшем показаны, в общих чертах, несколько типов синтеза, механохимически активированных на макромолекулярных основаниях (гомо- или гетероцепных полимерах) или даже исходя из веществ с малыми молекулами (мономеров).

2. Механохимическая прививка и блоксополимеризация

Одно из экспериментальных направлений в области механохимического синтеза было основано на образовании радикальных центров в механодиструктивном процессе, инициатором винильной полимеризации будучи прививка-блоксополимеризация работая в системе полимер : мономер или полимер : полимер [1]...[6].

В первом варианте были использованы в качестве „суппорта" для прививки полиэтилентерефталат и полиамиды (в особенности поли-ε-капролактам), а в качестве винильных компонентов использовались винилхлорид в газообразном состоянии, акрилонитрил, винилацетат, или стирен.

Рис. 1 показывает изменение химического состава полимерасуппорта в том случае, когда в качестве исходного вещества используется поли-ε-капролактам, а в качестве способа активации виброразмол. Кривые *1...3* описывают увеличение содержания полимера, введённого пу-

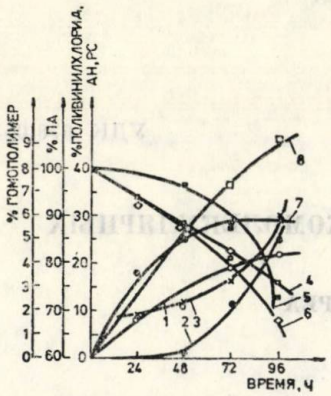


Рис. 1. — Механохимическая прививка поли-ε-капролактама с винильными мономерами : *1* — химически связанный полимер в %, в прививке с винилхлоридом ; *2* — с акрилонитрилом ; *3* — со стиролом ; *4*—супорт, % ПА, в прививке с винилхлоридом ; *5*—с акрилонитрилом; *6*—со стиролом ; *7* — гомополимер в %, в прививке с винилхлоридом ; *8* — со стиролом.

тём привывки (поливинилхлорида, полиакрилонитрила, полистирола), а кривые *4*...*6* изображают уменьшение содержания полимера-суппорта. Во всех случаях реакция гомополимеризации остаётся второстепенным процессом (кривые *7*, *8*), а иногда даже совсем не имеет места (прививка с акрилонитрилом) [4], [6].

Проводя прививку полиэтилентерефталата при низких температурах (примерно минус 75°С) акрильными и метакрильными кислотами, путём виброразмола, возможно введение значительного числа полярных кислотных групп, чуствительно увеличивающих гидрофильность первоначального полимера [5].

Реакции прививки — блоксополимеризации возможны и путём механической одновременной обработки двух или нескольких макромолекулярных компонентов. В качестве источника активации использовалась механическая энергия получения виброразмолом, мастикацией на пластографе Брабендера, вальцованием, а компонентами реакции были использованы системы: полиэтилен — поли-ε-капролактам, полиэтилен—этилцеллюлоза, поливинилхлорид—синтетический каучук. В некоторых случаях источником активации служил и виброразмол в инертной среде, при низких температурах (—40°...70°С) и небольшой продолжительности (5...40 мин.).

Некоторые из полученных результатов по блоксополимеризации полиэтилена с поли-ε-капролактамом при виброразмоле показаны на рис. 2, изображающей зависимость между отношением вышеуказанных компонентов реакции и степенью конверсии (Х%, кривая *1*), содержанием растворимой фракции (Р.ч. %, кривая *2*) и процентным содержанием азота (Н%, кривая *3*, *4*), введённого в новый полимер посредством реакции прививки—блоксополимеризации. Установлено, что по мере увеличения процентного содержания азота в фракции, экстрагированной растворителями, характерными для полиамидов (рис. 2, кривая *3*), увеличивается содержание фракции, представляющей полимер, растворимый в растворителях суппорта, а степень превращения

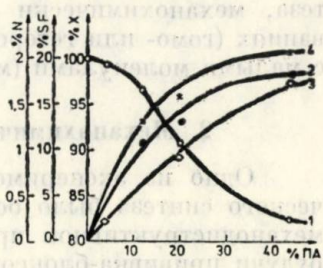


Рис. 2. — Механохимическая блоксополимеризация полиэтилена с поли-ε- капролактамом посредством виброразмола: нерастворимая часть: *1* — % Х степень полимеризации ; *2* — % N-изменение азота ; растворимая часть : *3*—% SF-растворимая часть; неэстрагированный образец — *4*—%N-изменение азота.

в сополимер (X%—кривая *1*) уменьшается. Отсюда следует, что фракция, изменение которой описано кривой *2*, не представляет собой исключительно полиэтилен, а его сополимер с поли капролактамом.

Изучение влияния температуры (+18°...−40°C) на эту реакцию показывает что она подверждается выгодному влиянию при наименьшем значении этого фактора влияния.

Надо подверкнуть, что у получаемого сополимера в значительной степени уменьшается растворимость и коэффициент текучести, последний убывая от 1,24 (значение этого коэффициента в полимере-суппорта, до 0,35). Эти результаты показывают что основные реакции (реакции прививки и сополимеризации) усложняются процессами сшивании. Впрочем, размол полиэтилена одинаковых условиях указывает такие же эффекты. Следовательно, изменения, произведённые виброразмолом этого макромолекулярного продукта при низких температурах, не являются исключительным образом изменениями типа деструкции, а комбинируются с реакциями сшивания.

Другая система образованная из полиэтилена и этилцеллюлозы была подверждена обработке на пластографе Брабендера при температуре 165°C, в воздухе. Полученный блоксополимер, после удаления оставшевося после реакции излишка этилцеллюлозы путем экстрагирования соответствующими растворителями, имеет ряд свойств, изменённых по сравнению с свойствами полимера суппорта. Можно считать, что значения физико-механических показателей остаются близкими к соответствующим значениям исходного полиэтилена (рис. 3, кривые *1*...*4*), за то новый продукт имеет более хорошие диэлектрические свойства : диэлектрическая постоянная увеличивается (рис. 3 кривая *5*), а тангенс угла потерь уменьшается (рис. 3, кривая *6*) [7].

Наконец, укажем ещё один пример, относящийся к блоксополимеризации поливинилхлорида с некоторыми эластомерами (ЭУРОПРЕН и КАРОМ). Важнейшим результатом, полученными при изменении этим способом поливинилхлорида (используя рецептуру для жёсткого ПВХ), было увеличение сопротивления удару. На рис. 4 изображена зависимость этой величины (a_k) от изменения процента хлора, обусловленного введением в структуру полимера переменного количества вулканизированного и невулканизированного эластомера (ЭУРОПРЕН и КАРОМ) [6].

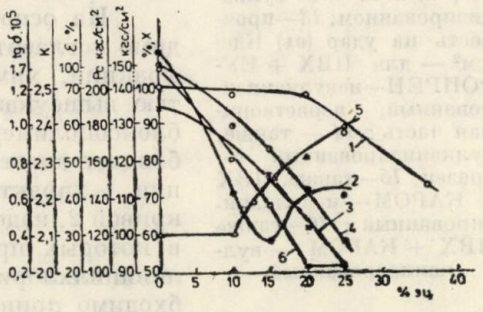


Рис. 3.—Изменение некоторых свойств полиэтилена посредством механохимической блоксополимеризации с этилцеллюлозой, на пластографе Брабендера: *1*–%X-степень превращения ; *2*— Pc—прочность на разрыв ; *3* — максимальный предел текучести; *4* — ε%-растяжение на разрыве; *5* — *k* — диэлектрическая постоянная ; *6* — tg δ .10⁶ — тангенс угла диэлектрических потерь.

Сомастикация обоих компонентов, введённых в различных пропорциях, на валках, при температуре 170°C, приводит во всех

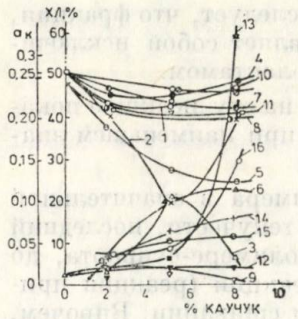


Рис. 4.—Изменение процентного содержания хлора и убарной прочности с отношением компонентов в случае блоксополимеризации поливинилхлорида и каучука (ЕУРОПРЕН и КАРОМ, вулканизированных и невулканизированных) посредством сомастикации на валках : ПВХ и ЕУРОПРЕН— невулканизированный : % хлора (% Cl) в исходном образце ; *2* —в нерастворимой части; *3* — в растворимой; *4* ... *6*— также, в вулканизированном образце ; ПВХ + КАРОМ : *7*...*9*, в невулканизированном образце ; *10* ... *12* — в вулканизированном; *13*—прочность на удар (a_k) Кде/ /см^2 — для ПВХ + ЕУРОПРЕН—невулканизированный, нерастворимая часть ; *14* — также, вулканизированный образец; *15*—также, ПВХ + КАРОМ — невулканизированный ; *16*—также ПВХ + КАРОМ — вулканизированный.

случаях к получению двух фракций: одной растворимой и другой нерастворимой в бензоле (растворителе, употребляющемся для удаления возможных следов оставшегося после реакции каучука). Изменение процентного содержания хлора в полученных блоксополимерах сравнивалось с аналогичным изменением в физических смесях, полученных в тех же условиях, но без вальцовки (рис. 4, кривые *1*, *4*, *7*, *10*).

В сополимере, полученном одновременной со-мастикацией поливинил хлорида с переменными количествами но не больше 5% невулканизированного ЭУРОПРЕНА, можно обнаружить значительное уменьшение процентного содержания хлора по мере увеличения количества эластомера, с достижением минимум (рис. 4, кривая *2*). В том случае, когда в реакционной смеси процент содержания эластичного компонента увеличивается, можно наблюдать значительное изменение состава полимера: количество химически связанного хлора уменьшается в значительной степени (ветви кривой *2* после минимума). В растворимой фракции изменение этого параметра имеет обратный характер, с достижением максимума для хлора (позиция которого совпадает с позицией предыдущего минимума). Совершенно аналогично проведённые опыты с румынским каучуком КАРОМ показывают то же направление влияния эластичной компоненты с той лишь разницей, что минимум и максимум менее резки (кривые *8*, *9*).

На основании полученных данных необходимо согласиться с фактом, что нерастворимые фракции, химический состав которых описан частью вышеуказанных кривых представляют собой блоксополимеры, в которых количественно преобладает эластичная компонента; напротив, фракции, характизированные восходящей ветвью кривой *2*, надо рассматривать как блоксополимеры в которых преобладает жесткая компонента (поливинилхлорид). Для растворимых фракций необходимо принимать обратные составы.

Выводы, вытекающие из этой интерпретации хорошо согласуется с результатами, полученными при определении ударной прочности-максимумами, выявляющими значительные увеличения у блоксополимеров нерастворимых в бензоле (кривые *13*, *15*).

При введении в реакцию тех же эластомеров (но вулканизированных и при изучении тех же параметров (изменении процентного содержания хлора и ударная прочность), можно наблюдать качественно аналогичные результаты, отличающиеся количественно. В общим, измене-

ния, полученные для величин, рассматриваемых как критерии, происходят более медленно по сравнению с изменениями, специфичными блоксополимерам, полученным в идентичных условиях, но с невулканизированным эластомером. Максимумы и минимумы, ясно выраженные в первом случае, достигаются во втором случае, вероятно при составах, расположенных вне тех, которые были рассмотрены нами (кривые *5*, *6* и *11*, *12* по сравнению с кривыми *3*, *4* и *8*, *9*). Ударная прочность возрастает и в том случае у блоксополимеров, нерастворимых в бензоле (кривые *14*, *15*).

Полученные данные позволяют утверждать, что при помощи сомастикации этих двух компонентов в условиях, специфичных для промышленной технологии обработки, можно изменить в положительном направлении некоторые физико-механические показатели, в особенности ударную прочность.

3. Механохимическая поликонденсация

Исходя из того, что вследствие механохимической деструкции гетероцепных полимеров, по мере эволюции процесса и создания благоприятных условий накапливается растущее число функциональных групп, что вдоль магистральной трещины концентрируются такие группы, мы поставили себе задачу их полезного использования в реакциях, названных нами „механохимической поликонденсацией". В качестве основы были использованы полиэтилентерефталат, полиамиды, целлюлоза, поливиниловый спирт [3], [8]...[14].

На модели полиэтилентерефталата, который при деструкции вследствие виброразмола при температуре среды (или более низкой) даёт растущее число карбоксильных групп, была осуществленна реакция с рядом алифатических и ароматических диаминов. Из рис. 5 можно сделать вывод, что химическое связывание использованного диамина (этилендиамина) коррелируется с величинами, характеризующими механодеструктивный акт, при помощи которого осуществляется этот синтез. Так, процентное содержание азота, связанного к цепям основы при помощи реакции с диамином, хорошо согласуется с числом расщеплённых связей (рис. 5, кривая *1*), следовательно, с числом образованных активных фрагментов (кривая *2*), с кислотным числом, изменяющим растущее число карбоксильных групп (кривая *3*), связанное с уменьшением молекулярного веса (кривая *4*).

Механохимическая реакция между фрагментами деструкции полимера суппорта и использованными диаминами имеет как ре-

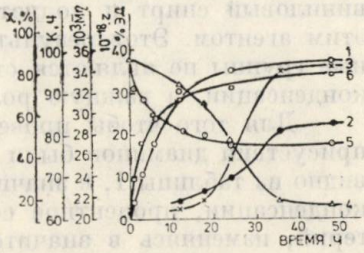


Рис. 5. —Изменение степени превращения и вышедшего в реакцию количества этилендиамина с продолжительностью размола, сравнительно с числом расщеплённых связей (z), вискозиметрическими молекулярных весов (M_η) и числом кислотности (СА) : *1* — количество этилендиамина, вошедшее в реакцию; *2* — число расщепленных связей ; *3* — число кислотности; *4* — молекулярный вес ; *5* — степень превращения в нерастворимый продукт; *6* — степень превращения в растворимом продукте.

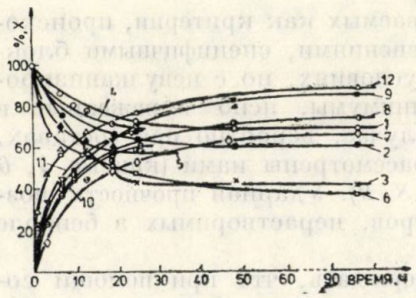


Рис. 6.— Изменение степени превращения (X%) в нерастворимые и растворимые продукты, полученные из фрагментов деструкции полиэтилентерефталата прореагировавшиеся с хексаметилендиамином, соответственно этилендиамином, в зависимости от продолжительности виброразмола : *1...3* — степени превращения (% X) для нерастворимой части из продуктов с хексаметилендиамином ; *4...6* — из продуктов с этилендиамином ; *8...9* и *10...12*, соответственно в растворимой части.

зультат получение двух фракций—одной нерастворимой и другой растворимой —изменение которых в зависимости от продолжительности обработки описывается кривыми *5*, *6*. Рис. 6 (кривые *1...3*; *7...9*) показывают, что первая количественно убывает по мере увеличения продолжительности процесса; напротив, вторая фракция количественно возрастает (кривые *4...6*, *10...12*). Но в обоих случаях достигается предел степени превращения X.

На этой реакции, как и на всякое превращение механохимического происхождения снижение температуры оказывает благоприятное влияние. Реакции этого типа могут начинаться под действием различных форм механохимической энергии : виброразмола, ультразвука, криолиза и.т.п. Более того, реакция может быть осуществлена и при воздействии других форм энергии, например тепловой, или при облучении лучами γ Co^{60}. [11].

Было показано что полиэтилентерефталат, полиамиды, целлюлоза фиксируют значительные количества диамина, в то время как поливиниловый спирт и полиэтилен реагируют лишь в небольшой мере с этим агентом. Этот результат привёл к заключению, что функциональные группы не являются строго ответственными за реакцию с агентами конденсации, а важную роль играют активные центры.

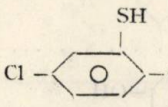
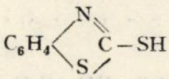
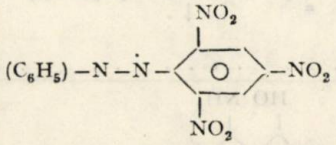
Для того чтобы проверить существование радикальных центров в присутствии диаминов были введены различные акцепторы, которые, как видно из таблицы 1, в значительной мере пертурбируют фиксацию агента конденсации, процентное содержание азота, рассматриваемое как критерий, изменяясь в значительных пределах. Изучение использованных акцепторов позволило установить, что некоторые из них играют роль ускорителей реакции с диаминами (кислород и окись азота), а другие— роль замедлителей (фенол).

Полученные результаты доказывают присутствие радикальных центров в таких системах реакции и их роль. На этом основании, как и на основании сообращения что полиэтилен, который не в состоянии получить путём деструкции активные функциональные группы, вступает всё же в реакцию с диаминами, было следано заключение что последние могут выступать как радикальные акцепторы. Надо согласиться с тем, что этот путь способствует хотя бы частично протеканию реакции „механохимической поликонденсации".

Более подробные исследования были проведены с полиэтилентерефталатом, для которого были найдены условия либо для непосредственной реакции с диаминами, либо для проведения этой реакции при посред-

Таблица 1

Влияние радикальных акцепторов на механохимическую реакцию поликонденсации между полиэтилентерефталатом и этилендиамином

Отношение между компонентами	Природа акцептора	Химическая формула акцептора	Продолжительность синтеза*) часы	Процентное содержание химически связаного азота [%]
Полиэтилентерефталат : этилендиамин 1 : 1 (гравиметрически)	—	—	9	6,7
	—	—	24	16,0
	Дихлортиофенол		9	5,0
			9	5,54
	β-нафтол	$C_{10}H_7OH$	9	4,95
	Хидрохинон	$HO-C_6H_4-OH$	9	6,6
	Додецил меркаптан	$C_{12}H_{25}SH$	9	4,1
	2-меркаптобензотиазол			
	Дифенилпикрилхидразил		24	14,0
	Молекулярный кислород	O_2	9	8,6
	Окись азота	NO	9	8,9
	Фенол	C_6H_5OH	9	2,25

*) Температура : 18°C ; процент наполнения : 0,4%.

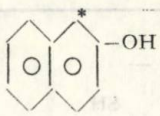
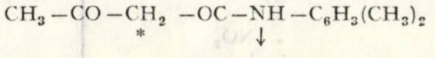
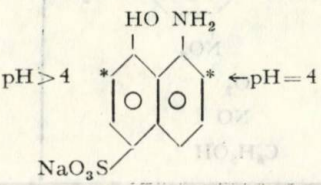
ствии кислых хлоридов (например, хлористого себацила). Полиамиды могут претерпевать аналогичные превращения не только при помощи реакции с диаминами, но и при помощи этиленгликоля, фенола, дикислот [15].

Полученные этим путём полимеры (нерастворимые фракции) термостабильны, стойки к действию химических агентов, обладают полупроводниковым характером и могут быть рекомендованы для прямого употребления в целях, в которых необходимы вещества с такими характеристиками, или же могут употребляться как посредники в других реакциях.

Так, вещества полиэфир—полиамидного типа, полученные из полиэтилентерефталата с различными ароматическими диаминами, могут быть превращены диазотированием и присоединением красителей (типа тех, которые указаны в таблице 2) в цветные полимеры. В том случае когда в качестве присоединяемых компонентов используются вещества,

Таблица 2

Присоединяемые компоненты, употребляемые для синтеза цветных полимеров

Присоединяемые компоненты		pH раствора присоед. комп.	Осуществляемый цвет*)
Наименование	Формула		
β-нафтол		pH > 7 (присоединение в*)	Красный
Резорцин		pH > 7 (присоединение в *орто-* или *пара* по отношению к —OH)	Жёлтый
Нафтол (диацетил-ацетоно-толуидин)		pH > 7	Жёлтый
Кислота		pH ≥ 4 первое присоединение в pH = 4 ; второе присоединение в pH = 8	Фиолетовый (после двух последовательных присоединений)

*) Полимер был употреблен в порошкообразной форме.

содержащие в свою очередь первичные аминные диазотируемые группы, возможно регулирование оттенка по желанию [15].

С другой стороны, ввиду того что продукты, полученные механохимической поликонденсацией, содержат вдоль макромолекулярной цепи электроотрицательные атомы, как например азот, кислород, содержщаие электроны, не участвующие в химической связи, стало возможным использование этих продуктов в качестве лигандов в реакциях комплексообразования.

4. Механохимическая комплексообразование

Для синтеза полихелатов состоящих из макромолекулярных лигандов представляющих собой продукты механохимической поликонденса-

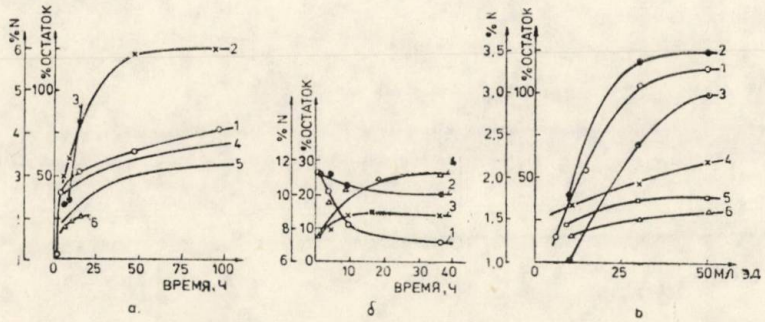


Рис. 7 *а*—Изменение процентного содержания азота и термостойкого остатка с продолжительностью размола в комплексах полиэтилентерефталата с этилендиамином и различными металлическими солями : *1* — изменение содержания азота в комплексе с хлорным железом ; *2* — также, с хлорным марганцем ; *3* — также с ацетатом марганца ; *4*—изменение термостойкого остатка в комплексе с хлористым железом ; *b* — Изменение процентного содержания азота и термостойкого остатка с продолжительностью размола : *1*—изменение процента азота в комплексе с хлористым железом, полученным в присутствии этилендиамина ; *2* — тоже, с ацетатом марганца ; *3* – тоже, с хлорным марганцем ; *4...6* —соответствующие изменения термостойкого остатка.

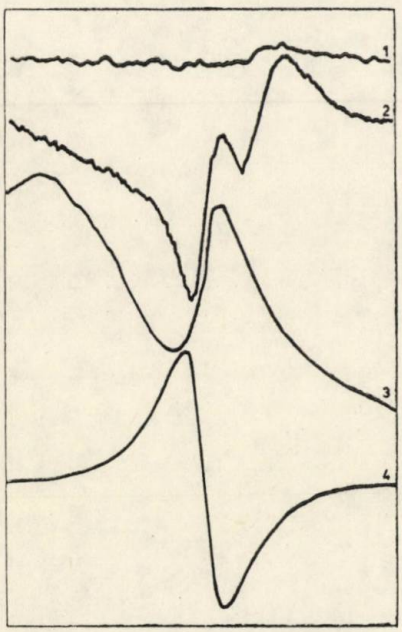


Рис. 8.—Спектры ЭПР для нерастворимого комплекса, из полиэтилентерефталата (1) е: *2*—этилендиамином и ацетатом марганца ; *4...6* — соответствующие изменения термостойкого остатка.

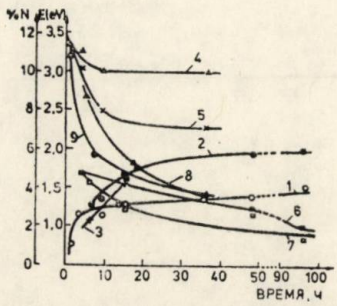
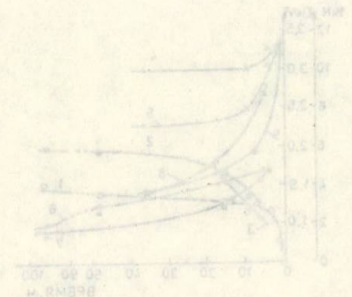
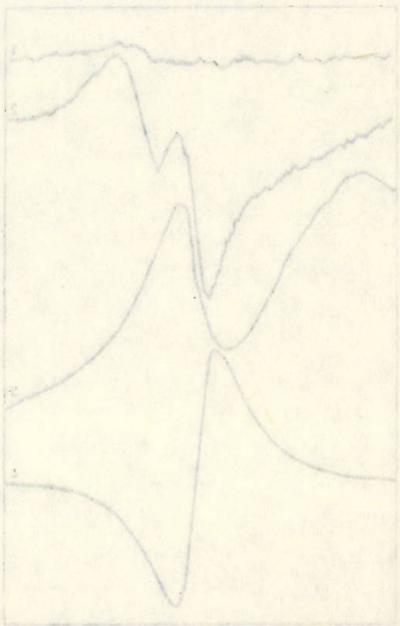


Рис. 9.— Изменение энергии активации удельной электропроводности с процентом азота, введённого в комплекс посредством изменения продолжительности или количества этилендиамина: *1*—полиэтилентерефталатный супорт с $FeCl_3 . 6H_2O$; *2*—тоже, с $Mn(CH_3COO/2 . 4H_2O)$; *3* — тоже, с $Mn.Cl_2 . 4H_2O$; *3*—поли-ε-капролактамный супорт с хлорным железом и этилендиамином ; *4*, *5* — тоже без этилендиамина ; *6*, *7* — изменение электропроводности *E* (eV) в образцах *1*, *2* ; *8*, *9*—соответственно *4*, *5*.





ции фрагментов деструкции, получающихся от различных макромолекулярных соединений (полиэтилентерефталата, полиамидов, целлюлозы, белок и.т.п.) с разнообразными диаминами, были использованы как комплексообразающие центры примущественно Fe^{3+}, Mn^{2+}, V^{3+}, происхождение из соответствующих металлических солей. Источниками механической активации служили : виброразмол, ультразвучивание или криолиз. Реакция комплексообразования была проведена одновременно с синтезом лиганда [6], [10], [14]...[19].

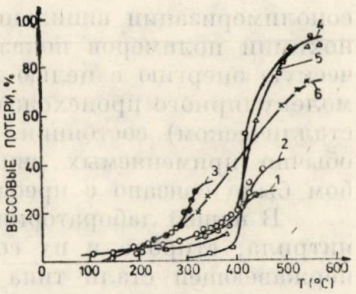


Рис. 10. — Изменение потерь веса с температурой разложения для : *1*—комплекса полиэтилентерефталата с $FeCl_3 . 6H_2O$; *2* — тоже, с $MnCl_2 . 4H_2O$; *3*—тоже, $Mn(CH_3COO)_2 . 4H_2O$; *4*—комплекса с поли-ε-капролактамом с этилендиамином и $FeCl_3.6H_2O$; *6*—тоже, без этилендиамина.

Химическое связывание металла учитывалось как изменением процента азота, который в комплексе уменьшается сравнительно с полученным в тех же условиях поликонденсатом, так и количеством термостабильного остатка, полученного сжиганием при 1 000°C.

Изменение этих характеристик в комплексах на основе полиэтилентерефталата и поли-ε-капролактама, в зависимости от продолжительности или количества агента конденсации, показано на рис. 7. Видно что при возрастании продолжительности или количества агента конденсации, содержание термостабильных остатков возрастает, а анализ ИК показывает существование полос, общих с полосами лиганда (соответственно поликонденсата).

Введение металла в структурную единицу макромолекулярных соединений этого типа существенно изменяет некоторые их свойства по сравнению со свойствами полимера-суппорта. Например, полиэтилентерефталат, превращённый в комплекс с помощью диаминов и металлических солей, теряет характер изолятора, становясь полупроводником, факт, установленный при помощи спектроскопии ЭПР. Полученные спектры доказывают ясно решенными сигналами что механохимически синтетизированные полихелаты обладают постоянным магнитным моментом (рис. 8). Кроме того, значения энергии активации удальной электропроводности зависит от химического состава комплекса и изменяются с температурой в интервале $10^{-12}...10^{-1}$ ом $.см^{-1}$ (рис. 9). Изменение весовых потерь в зависимости от температуры (определённой термогравиметрическим способом) показано на рис. 10 и харакеризует эти полимеры как термостойкие материалы.

Таким образом удалось впервые осуществить механохимическимпутём полихелатов — продуктов синтез поликонденсации полиэтилентерефталата, поли-ε-капролактама (или неизменной полиамиды), целлюлозы с различными диаминами (в особенности с этилендиамином) выполняющими роль макромолекулярных лигандов.

5. Механохимическая гомо- и сополимеризация

Другой тип синтеза, исследуемый нашей лабораторией в последнее время основывается на механической активации полимеризации и

сополимеризации винильных мономеров. Исследования в области механохимии полимеров показали что для того чтобы перенимать механическую энергию с целью их активации, вещества должны быть макромолекулярного происхождения или находится в конденсированном (кристаллическом) состоянии. По этой причине, гомо- и сополимеризация обычно применяемых винильных мономеров механохимическим способом было связано с преодолением ряда проблем.

В нашей лаборатории удалось провести полимеризацию акрильного нитрила, стирола и их сополимеризацию виброразмолом в сосудах из нержавеющей стали типа V_2A, без введения какой-либо прибавки, с продолжением продолжительности работы до приблизительно 200 часов и с сохранением постоянного значения процента наполнения ($\eta = 1\%$).

И этот тип синтеза даёт два сорта продуктов : растворимых и нерастворимых в обычно употребляемых растворителях, специфичных для соответствующих полимеров обычного производства.

Элементарный анализ механически синтетизированных растворимых гомополимеров и сополимеров показал присуствие значительных количеств термостойкого остатка.

В исследованном интервале, этот остаток изменяется с временем согласно кривым *8...10*, что доказывает химическое присоединение металла в структурных этих полимеров.

Анализ лучами X показал, что эти продукты кристалличны, кристалличность достигая определённого максимума, после которого начинает падать (кривая *11*).

Необходимо подчеркнуть что путём выбора оптимальных условий—больших продолжительностей обработки, малых значений коэффициента заполнения—удалось получить при температуре $18 \pm 2°C$ степени превращения равное 82,5% для гомополимера и даже 100% для сополимера.

Первые информации о структуре и свойствах этих макромолекулярных соединениях были получены из данных элементарного анализа, спектроскопии ИК, ЭПР, спектроскопии Мёсбауэра дифференциального термического анализа, определении растворимости и интервала смягчения.

Анализ ИК-ого спектра, полученного в случае гомополимера, указывает на присуствие полосы 2 250 $см^{-1}$, характерной для группы $-C \equiv N$, но представляется интерес тот факт, что по сравнению с эталоном появляется ещё и ряд новых полос, а именно при 850 и 1 150 $см^{-1}$, которые могут быть приписаны связи $-C=N-$, при 1 380 и в особенности при 1 650 $см^{-1}$, которые определяют связи $-C=C-$, $-C=N-$, расположенные в коньюгированной системе. Наконец, полосы поглощения при 2 060 и 2 180 $см^{-1}$, которые также не встречаются в эталонной пробе, могут быть приписаны железу, химически связонному в этих продуктах.

Помимо элементарного анализа и спектроскопического ИК анализа, химическая фракция металла в структурных единицах новых продуктов была доказана также и при помощи спектроскопии Мёссбауэра. Спектры представленные на рис. 11 (кривые *2* и *3*) показывают что железо вошло в химическую связь и что в форме отдельных фаз можно обнаружить лишь слабые следы железа. Кроме того, спектры

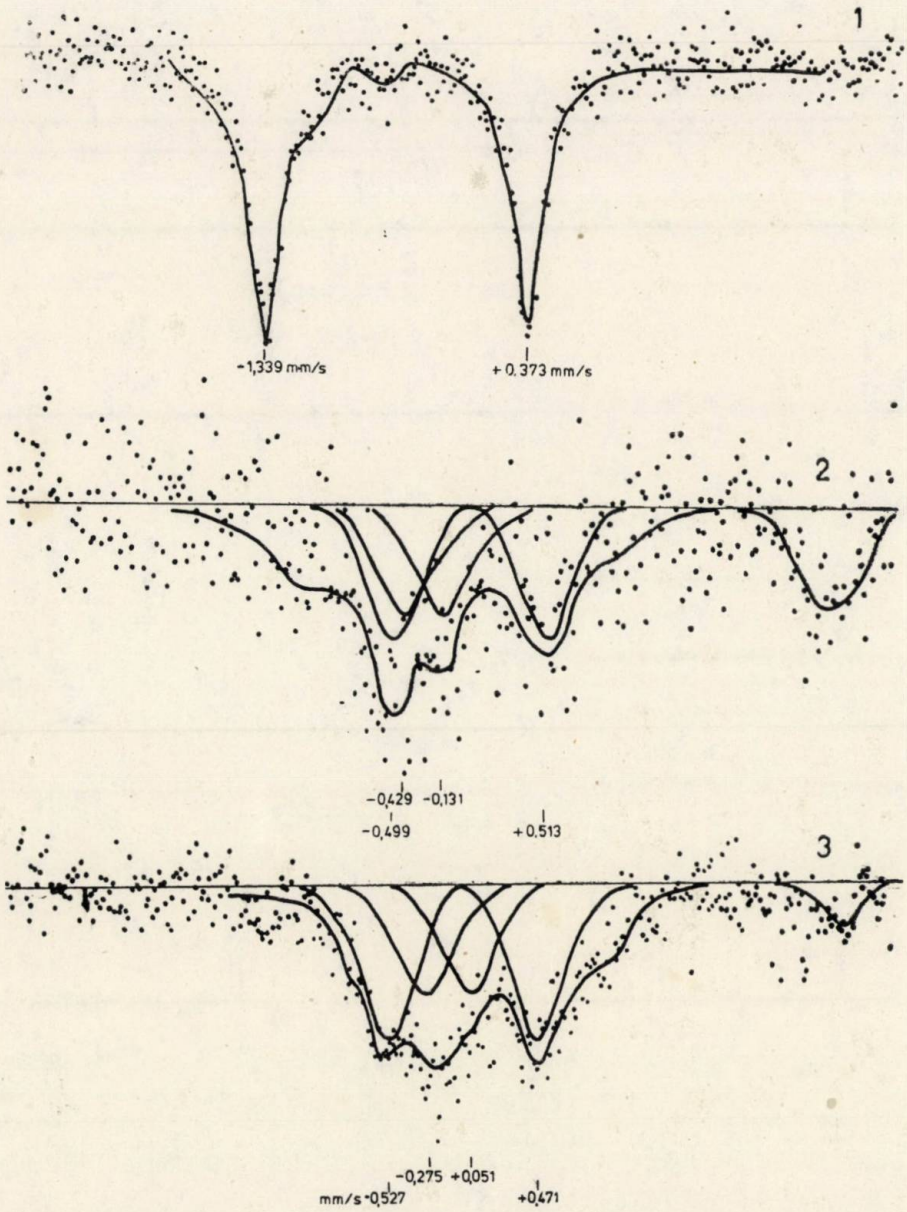
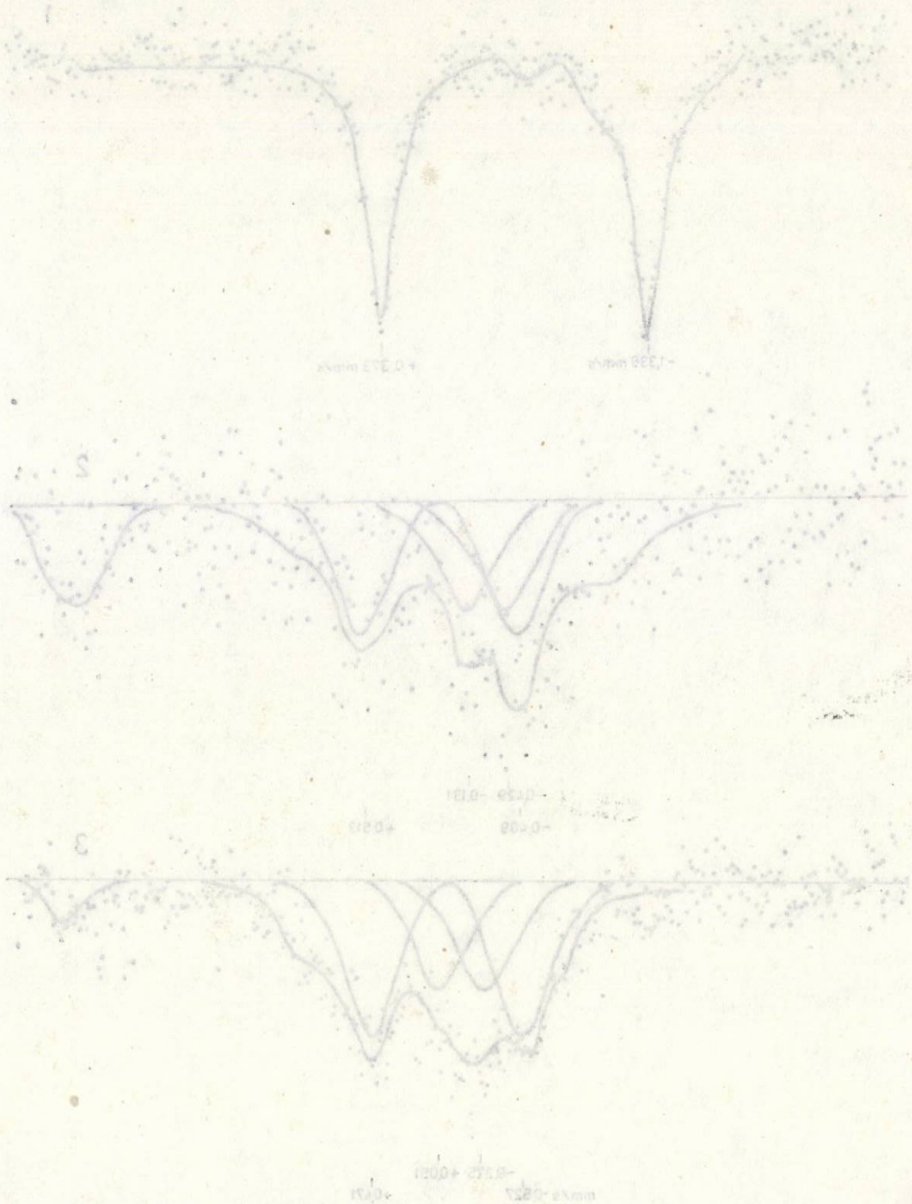


Рис. 11.— Спектры Мёссбауера снятые для механохимически синтетизированных гомополимеров ; *1* — эталон (нитропрусият натрии) ; *2* — полиакрилнитрил ; *3* — полистирол.


1
2
3

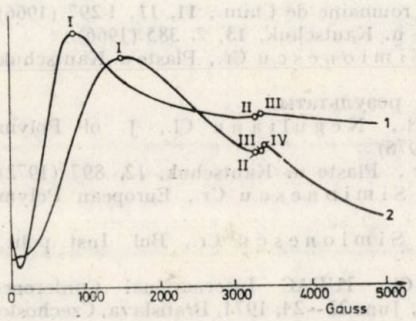


Рис. 12— Спектры ЭПР, снятые для механохимически синтетизированных гомополимеров : *1*—полистирол: *I* — *H*, [gauss] — 816,32 ; g = 8,33 ; *II*—3 116,30; g=2,18 ; *III*—3 367,32 ; g = 2,02 ; *IV* — ; *2* — полиакрилонитрил: *I*—*H*, [gauss]: 1 428,58 ; g = = 4,70 ; *II* — 3 265,28 ; g = 2,08 ; *III* — 3 316,60 ; g = 2,05 ; *IV* — 3 367,32 ; g = 2,019.

ЭПР, снятые для этих продуктов показывают существование иона Fe^{3+} в поле с большой симметрией, что доказывает лишний раз химическую фиксацию металла в структурных единицах полимера (рис. 12).

Поведение гомо- и сополимеров, синтетизированных механохимически этим способом, при увеличении температуры, было исследовано при помощи термогравиметрического анализа, проведённого в воздухе при изменении температуры до 900°C. Любое из исследованных веществ не теряет более 20% при температуре до 400°C, а гомополимер на основе акрилонитрила, растворимая в ДМФ фракция, практически не испытывает никаких превращений при температурах ниже 246°C.

Учитывая всю информацию, полученную при проведённых анализах, необходимо приписать важную роль в инициировании этого типа полимеризации стенке аппарата или металлу, отделяющемуся в виде тонких частиц при ударах размалывающих шариков о стенки реакционного сосуда при коррозивном действии мономера.

На основании полученых результатов можно утверждать, что полимеризация начинается на активных центрах металлической поверхности. В начальном этапе (до примерно 48 часов) кинетическая энергия удара, развиваемая виброразмолом, потребляется главным образом для активации металлических частиц, а также и для возбуждения электронов на поверхностных структурах атомов, принадлежащих металлу. Определённые сильно активированные поверхности могут, при контакте с винильным мономером, фиксировать его, инициируя полимеризацию. С другой стороны необходимо согласиться и с „вырыванием“ возбуждённых электронов с металлической поверхности, образованием электронных потоков, способных, в свою очередь, инициировать полимеризацию.

Полученные данные позволяют также приписать определённую роль в протекании полимеризации и группе —C≡N. Наконец, вид полученных кривых указывает на то, что параллельно с механосинтезом активируются и механодеструктивные процессы.

Поступило 27 мая 1981 г.

Ясский политехнический институт,
Кафедра органической и
макромолекулярной химии

ЛИТЕРАТУРА

1. Vasiliu-Oprea Cl., *Über mechanochemischen Abbau von Polyamiden während der Schwingmahlung und Herstellung einiger neuen makromolekularen Produkte.* Dokt. Diss., TH fur Chemie, Leuna, Merseburg, 1965.

2. Grohn H., Vasiliu-Oprea Cl., Revue roumaine de Chim., 11, *11*, 1297 (1966).
3. Grohn H., Vasiliu-Oprea Cl., Plaste u. Kautschuk, 13, *7*, 385 (1966).
4. Vasiliu-Oprea Cl., Negulianu Cl., Simionescu Cr., Plaste u. Kautschuk, 17, *9*, 639 (1970).
5. Vasiliu-Oprea Cl., Неопубликованные результаты.
6. Simionescu Cr., Vasiliu-Oprea Cl., Negulianu Cl., J. of Polym. Sci., Polymer Simposium, 64, 149 (1978).
7. Vasiliu-Oprea Cl., Simionescu Cr., Plaste u. Kautschuk, *12*, 897 (1972).
8. Vasiliu-Oprea Cl., Negulianu Cl., Simionescu Cr., European Polym. J., 6, 181 (1970).
9. Vasiliu-Oprea Cl., Negulianu Cl., Simionescu Cr., Bul. Inst. polit., Iaşi, XV (XIX), *3—4*, 45 (1969).
10. Simionescu Cr., Vasiliu-Oprea Cl., IUPAC International Conference „Chemical Transformations of Polymers", June 22—24, 1971, Bratislava, Czechoslovakia, vol. III, 75.
11. Simionescu Cr., Vasiliu-Oprea Cl., Negulianu Cl., Makromol. Chem., *163*, 75 (1973).
12. Simionescu Cr., Vasiliu-Oprea Cl., Negulianu Cl., European Polym. J., 10, 61 (1974).
13. Simionescu Cr., Vasiliu-Oprea Cl., Nuova Chimica, 48, *11*, 91 (1972).
14. Vasiliu-Oprea Cl., *Mechano-chemische Reaktionen auf einige Homopolymere*. Mitt. an dem Seminar von 29 Nov. 1974 Deutsches Kunststoff Institut, Darmstadt.
15. Simionescu Cr., Vasiliu-Oprea Cl., Adv. in Chem. Series, *128*, 68 (1973).
16. Симионеску К., Василиу-Опря К., Негуляну К., *Механохимические активированные комлпексообразование из полиэтилентерефталата, хлорида железа и этилендиамина*. Сообщение на 39-го Съезда по пром. хим., 7—11 септ., 1970, Бухарест, 12/169.
17. Simionescu Cr., Vasiliu-Oprea Cl., Negulianu Cl., Die makromol. Chem., *148*, 155 (1971).
18. Simionescu Cr., Vasiliu-Oprea Cl., Negulianu Cl., Рум. пат. Nr *69 467* (1972).
19. Simionescu Cr., Vasiliu-Oprea Cl., Negulianu Cl., Angew. macromol. Chem., 44, 17 (1975).

SINTEZA MECANO-CHIMICĂ A COMPUŞILOR MACROMOLECULARI

(Rezumat)

Se discută rezultatele de bază obţinute în ţara noastră în domeniul sintezei mecano-chimice a polimerilor. Cercetările în acest domeniu abordează o serie de probleme fundamentale privind sinteza mecano-chimică prin grefare—bloccopolimerizare, policondensare şi complexare, precum şi homo- şi copolimerizare a unor monomeri vinilici. Pentru activarea acestor reacţii s-a folosit măcinarea vibratorie, ultrasonarea, crioliza etc.

BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Tomul XXX (XXXIV), Fasc. 1—4, 1984
Secţia II
CHIMIE şi INGINERIE CHIMICĂ

RECENZII

BOOK REVIEWS РЕЦЕНЗИИ

RICHARDSON J. F., PEACOCK D. G., *Chemical Engineering*. Vol. III, sec. Ed. (SI Units), Pergamon Press Ltd., Oxford, 1979.

The third volume of the series *Chemical Engineering* edited by J. M. Coulson and J. F. Richardson, includes topics particulary important for the chemical engineering.

In the first chapter, entitled *Reactor Design — General Principles*, the authors discuss the classification of reactors, problems of chemical kinetics, general material and thermal balances for the main types of reactors and dimensioning principles, as well as the flow and the ideal mixing in chemical reactors.

The second chapter is devoted to the design of the catalytic reactors. Mass transfer within porous solids, chemical reactions in porous catalyst pellets in isothermal and non-isothermal conditions, chemical kinetics of heterogeneous catalytic reactions, design of the catalytic reactors in fixed and fluidised beds are treated.

In the third chapter the process control of chemical processes is discussed. After a survey of the sensitive elements, the types of controllers are presented, among them the pneumatic controllers (according to the control action type). The dynamic of the automation systems is treated by the help of the transfer function. Finally, the basic principles for the control and adjustment of feedback controllers are given.

The fourth chapter discusses general problems regarding the use of computers as well as the most important computation methods. After a short review of the digital computers, the FORTRAN program is discussed. Among the computation methods, the authors present the methods for solving the polynominal equations, the systems of linear simultaneous equations, the finite differences equations, the ordinary differential equations, the partial differential equations. To the end of this chapter, some methods for the optimisation of linear and non-linear objective functions are reviewed.

The fifth chapter is dedicated to the biochemical reactions engineering, the basic principles for the biochemical reactors design being presented.

The sixth chapter, entitled *Non-Newtonian Technology*, presents the differential equations of viscous fluids flow, fluid characteristics, analytical equations for flow in tube geometries, the influence of temperature and pressure on the flow and some equipments specific for these technologies.

In the seventh chapter the sorption process is studied. The main types of equipments for sorption processes, the equilibrium of these processes, the design of the sorption processes in fixed beds in isothermal and non-isothermal conditions are presented.

This book, as a whole, is a valuable handbook for all the specialists and students in chemical engineering, especially in what the chemical reactors design, chemical sorption processes, non-Newtonian technologies, the usage modern computation techniques in process control in chemical industry are concerned.

I. Grigoriu

HEBEISH A., GUTHRIE J. T., *The Chemistry and Technology of Cellulosic Copolymers*. Springer Verlag, Berlin–Heidelberg–New York, 1981, 351 pp.

The book, published by A. Hebeish and J. T. Guthrie, represents a synthesis of the grafted copolymers of cellulose with dienic and vinylic monomers.

The approaching made and content make this book particularly useful for the study of graftcopolymerization and chemical modification of cellulose.

The book contains 8 chapters, 351 pages, 91 figures and numerous references given for each chapter.

The chapter 1 presents briefly the essential notions of cellulose chemistry, preparation of synthetic polymers and copolymers.

In chapter 2 the principal methods of grafting vinylic monomers on cellulose are described. The methods of cellulose activation for grafting as well as the physical and chemical factors affecting the obtaining of cellulose macroradicals are taken into account.

The chapter 3 deals with the cellulose grafting by radiations. The processes of cellulose radiolysis, the physical and chemical modificatiens induced by different sources of high energy are described in detail.

The contribution of the authors to the systematization of an ample mondial literature deserves mention.

In chapter 4 the chemical activation of cellulose for grafting vinylic polymers is treated. The methods of grafting initiation by Ce^{IV}, V^{V}, Mn^{III} ions, oxygen–ozone mixture, IO_4^-, diazonium salts as well as the attack of free radicals on the unsaturated groups and the ionic mechanism (cationic, anionic) are described in detail. This chapter has a very reach scientific content.

An important method of cellulose grafting is described in chapter 6, namely the chemical modification by xanthogenation, acetylation, cyanoethylation, partial carboxymethylation, acrylamidomethylation, treating with of methylol acrylamide in alkali medium, carbamy ethylation, etc. followed by the activation of the new formed functional groups.

The characteristic properties and the industrial applications of the graft-copolymers are given in chapters 7 and 8.

The advantages and disadvantages of grafting processes are discussed critically referring to the physical and chemical properties and the using of the cellulose graft-copolymers obtained by different methods.

The book is written at a highly scientific level being particularly useful to the researchers working in the field of natural polymers, especially cellulose. It is based on a vast well systematized bibliography.

S. Dumitriu

VOWLES P. D., CONNELL D. W., *Experiments in Environmental Chemistry — A Laboratory Manual*. Pergamon Press, Oxford–New York–Toronto–Sydney–Paris – Frankfurt, 1980, 102 pp.

The book describes fourteen laboratory or field experiments in enviromental chemistry. The experiments have been divided into five parts. The first part, *Biochemical Processes in Aquatic Systems*, is basically concerned with the transformations of carbon, nitrogen, phosphorus and energy in aquatic systems. This gives a practical basis for discussion of a wide variety of aspects of Environmental Chemistry including photosynthesis, respiration, biogeochemical cycling primary production, plant nutrients, water quality, eutrophication and waste water-treatment. This part also provides the fundamental knowledge to develop further studies in the biological aspects of aquatic ecosystems.

In Part 2, *Toxic Substances in the Environment*, a wide assortment of environmental contaminats are considered in terms of their behaviour and occurence in various sectors of the environment. This section introduces gas chromatography, atomic absorption spectroscopy, thin layer chromatography, column chromatography and techniques for the measurement of atmospheric contaminants. It also includes a bioassay experiment in which the techniques for measurement of the toxicity of a substance are outlined. On this basis the environmental properties of insecticides, heavy metals, petroleum compounds and atmospheric contaminants can be discussed and developed.

In many ways Part 3, *Food Additives and Contaminants*, is similar to Part 2 but is specifically concerned with food and the occurrence of foreign substances which result from deliberate additions or other processes.

Part 4, *Chemical Ecology*, includes one experiment which is illustrative of the type of interaction involved in Chemical Ecology. This experiment leads to discussion of allelochemicals, pheromones, chemical defence substances and so on.

Part 5, *Stream Pollution*, is an integrative exercise in which a wide variety of information is collated and co-ordinated in relation to stream pollution.

Topics and methods have been designed to fit 3 to 6 hour laboratory times. Each experiment is accompanied by two to four questions that can be answered either from the experiment or by further reading; SI units are used throughout.

M. Macoveanu

AVERY H. E., SCHAW D. J. *Basic Physical Chemistry Calculations*. 2nd Edition, Butterworths a. Co (Publ.) Ltd, London – Boston – Sydney – Durban – Wellington – Toronto, 1980, 173 pp.

The initiative of Butterworth Group to republish a new edition of the above mentioned book was remarkable indeed. *Basic Physical Chemistry Calculations* surely is a very helpful book for both students and instructors. The purpose of the authors was to provide a source of informations having reasonable dimensions, mainly designed for the students in chemistry who intend to extend their fundamental knowledges in the field of physical chemistry. The book brings together nine fundamental topics in physical chemistry : (1) Units and Methods of Expression in Physical Chemistry, (2) Gases, (3) Thermochemistry, (4) Thermodynamics and Statistical Mechanics, (5) Solutions and Phase Equilibria, (6) Reaction Kinetics, (7) Electrochemistry, (8) Surface Chemistry and Colloids, (9) Molecular Structure, followed by Answers to Aditional Exemples and Appendix (Physical Constants, Conversion Factors, Relative Atomic Masses).

First chapter is intended to a concise but thoughtful survey of SI Units and their proper use in solving physical chemistry problems together with methods of expression in physical chemistry and several practical suggestions concerning the correct utilisation of physical quantities and their units. Then, the subsequent eight chapters each deal with a specified field of physical chemistry making use of typical carefully selected exemples followed by a certain number of unsolved exercises (answers given). Appendix refers mainly to some physical constants and conversion factors judiciously selected indispensable for solving physical chemistry problems.

This book, edited by Butterworths, can undoubtedly be recomended as a useful tool to a large circle of chemists eager to acquire a greater ability in handling physical chemistry calculations.

D. P. Lazăr

* * * *Probenahme, Theorie und Praxis*. Verlag Chemie, Weinheim, Deerfeld Beach (Florida), Basel, 1980, 384 S.

Das 9. Metallurgische Seminar des GDMB-Fachausschusses für Metallhüttenmännische Ausbildung (FMA), das in Zusammenarbeit mit dem Chemikerausschuß der GDMB Gesellschaft Deutscher Metallhütten und Bergleute vom 15. bis zum 17. März 1979 in Mönchengladbach veranstaltet wurde, stand unter dem für die mineralische Rohstoffwirtschaft im weitesten Sinne bedeutsamen Thema „Probenahme".

Das Buch enthält die Referate, die beim Seminar vorgestellt worden sind. In 18 aufeinander abgestimmten Referaten, sind die folgenden Themenkreise behandelt worden : *A* – Theorie der Probenahme und ihre wirtschaftliche Bedeutung (3 Beiträge) ; *B* – Probenahme an Erzen, Konzentraten und Zuschlagstoffen (4) ; *C* – Probenahme an festen und flüssigen Metallen (6) ; *D* – Probenahme an Flüssigkeiten und Schlämmen (2) ; *E* – Probenahme an Gasen und Abwässern (3).

In Zusammenhang mit dem Thema dieses Symposiums wurde ich z.B. mit dem folgenden Zitat des Prof. Dr. rer. nat. G. Kraft (Frankfurt/M) fündig :

„Obwohl die Probenahme, wie immer wieder von Praktikern mit Nachdruck betont wird, für die Güte einer Analyse von größter Bedeutung ist, findet man in den Lehrbüchern der chemischen Analyse über diesen wichtigen Gegenstand gar nichts oder so gut wie gar nichts, und dem entspricht auch ganz die äusserst mangelhafte Art und Weise, wie im Hochschulunterricht den Studenten Proben zur Analyse verabreicht werden bzw. wie die Studenten sich derartige Proben us einer g rösseren Menge aussuchen. Liegt das Material in Stücken vor, so wird einfach ein

Stück herausgefischt. Stimmen dann die Resultate der von verschiedenen Studenten ausgeführten Analysen nicht überein, so heißt es nur, daß der ein Stück mit mehr und der andere mit weniger Gangart erwischt hätte. Die völlig unzureichende Behandlung des wichtigen Problems der Probenahme in der wissenschaftlichen Literatur und dem Hochschulunterricht läßt den gerühmten innigen Kontakt zwischen Wissenschaft und Technik vermissen".

M. Macoveanu

EBERT K. H., DEUFLHARD P., JAGER W. (Ed.), *Modelling of Chemical Reaction Systems*. Springer Verlag, Berlin—Heidelberg—New York, 1981, 389 pp.

The volume includes the proceedings of an International Workshop, Heidelberg, Federal Republic of Germany, September 1—5, 1980. The intention of the workshop was to bring together mathematicians, physical chemists and chemical engineers, to shorten the process of development and application of new mathematical methods in practical chemical reaction systems.

To indicate the content of this valuable volume, the four parts are listed below, with the number of chapters and pages of each part in brackets :

Part I, Mathematical Treatment (ten chapters, 147 pp.),

Part II, Physical Chemical Applications (eleven chapters, 136 pp.),

Part III, Chemical Engineerig Applications (six chapters, 92 pp),

Part IV, Summary of the workshop (one chapter, 11 pp.).

Part I of the present volume includes ten articles about different typs of mathematical treatment of chemical reaction systems. The qualitative behaviour of chemical systems is studied by graph theoretic means, looking at the associated network structure, in Chap. 1 (O t h m e r) and Chap. 5 (F e i n b e r g). From this point of view, the authors analyze the possible occurrence and stability of multiple steady states. In Chap. 2 (O'M a l l e y) and Chap. 3 (H o p p e n s t e a d t, A l f e l d and A i k e n) singular perturbation techniques are disscussed. These are often successful in analysing chemical systems of moderate size. A new user-oriented simulation package for large chemical reaction systems is introduced in Chap. 4 (D e u f l h a r d, B a d e r and N o w a k). A survey of techniques for computing the sensivity matrices is presented in Chap. 6 (T i l d e n, C o s t a n z a Mc R a e and S e i n f e l d). Chap 7 (M i l s t e i n) and Chap. 8 (B o c k) are devoted to the actual identification of rate constants from experimental data (the „inverse problem"). Chap. 9 (K e e n e r) describes an analytic technique to study the entire periodic solution branch of a reaction system, and Chap. 10 (B o i s s o n a d e) presents a stochastic molecular dynamics technique for the investigation of fluctuations in non-equilibrium reaction—diffusion systems.

The first two papers of Part II (Chap. 11 — G o l d e n, Chap. 12 — W a r n a t z) point to constraints which must be considered in setting up reaction models for kinetic calculations. Polymer degradation (Chap. 13—E d d e r, B a s e d o w and E b e r t) and hydrocarbon pyrolysis (Chap. 16 — I s b a r n, E d e r e r and E b e r t) are treated as examples for huge systems. A special approach was proposed in Chap. 14 (K o c h). Attempts to model heterogeneous reactions are reported in Chap. 19 (C o m i n c i o l i, F a u c i t a n o, Ç e s c a). Combustion processes are treated from different aspects in Chap. 15 (P e t e r s) and Chap. 17 (V i d ó c z y, B o t á r, L u c á s, N e m e s, G á l). The best-known B e l o u s o v - Z h a b o t i n s k i reaction is further studied in Chap. 20 (G e i s e l e r, B a r - E l i) and Chap. 21 (N o s z t i c z i u s, F a r k a s).

A general survey of the present status of application of models in industry has been presented in the first paper of Part III (Chap. 22—E i g e n b e r g e r). The main contribution of the author consists of an attempt to answer the two fundamental questions : „Why do we do modelling and simulation?" and „How do we do it ?". Theoretical approaches of the dynamic behaviour of the chemical reactors are presented in Chap. 23 (L u s s) and Chap. 24 (G i l l e s and E p p l e) applied, further, in Chap. 25 (R a y), to the polymerization reactors. In Chap. 26 (K a h l e r t, R ä s s l e r and V a r m a), the chaos is predicted by dynamic simulation of a rather simple process : two consecutive first-order reactions, one exo- one, endotermic, in a continuous stirred tank reactor. In this case it is realy possible to say that modelling and simulation have predicted a chemical phenomenon.

Part IV (Chap. 28) is a summary, presented in conclusion of the workshop by R. N. N o y e s from his point of view of a physical chemist.

The intrinsic value of the articles included in this volume is enhanced by the great organizers' idea of a better cooperation between mathematicians, physical chemists and chemical engineers.

I. Siminiceanu

ÎNTREPRINDEREA DE ANTIBIOTICE
IAŞI
Telefon : (981) 4.27.70 ; Telex : 022244

THE ANTIBIOTICS ENTERPRISE
JASSY
Phone : (981) 4.27.70 : Telex : 022244

Nr. 6647 S. R. of ROMANIA produces and delivers new pharmaceutical formulae based on antibiotics (prescriptions) :

● SINERDOL EH-powder for drinkable solutions is a new type of semisynthetic antibiotic, it has a wide-ranging effect resulting from rifampicine being associated with natrium ethyl-hexanoate.

The pharmacokinetic, pharmacodynamic and pharmacotoxicologic properties of SINERDOL EH may be compared to those of rifampicine. Owing to its association with natrium ethyl-hexanoate, SINERDOL EH has an increased solubility in physiologic medial faster intestinal absorbtion, an improved enterohepatic recirculation and a drug considerably superior to the one achieved by original rifampicine along with a five times smaller hepatic toxicity.

The increased hydrosolubility and high stability—unlike original rifampicine—ensures the administration of extemporaneous drinkable solutions in precisely fractioned small doses, extremely useful in the treatment of tuberculosis in little and very little children.

The SINERDOL EH powder for the drinkable solution contains sugar and fragrance which provide a pleasurable taste, causing it to be easily accepted by children.

It is intended for the treatment of pulmonary tuberculosis, tubercular meningo-encephalitis in children of up to 14 years and in adults with gastric intolerance to rifampicine.

● SINTECLOX — injectable vials

Composition : ampicillin, associated with cloxacillin make up a wide-ranging bactericide with minimum toxicity.

It is intended for severe infections, prior to the identification of the pathogenic agent ;

— infections of the respiratory system, bronchopneumonia, post influenza, pneumonia a. o. ;

— infections of surgical and traumatic wounds ;

— septic abortions and puerperal infections ;

— septicaemia-infections in patients treated with imunosuppressors.

Prophilactic agent in general surgery.

Exporter : CHIMIMPORT—EXPORT, Bucureşti
B-dul Republicii nr. 10, sect. 4
R. S. ROMÂNIA

Tipărit sub cd. 31
la Întreprinderea poligrafică Iaşi,
str. 7 Noiembrie nr. 49

1985 MAJ 7

40822